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AIR POLLUTION: CONTROL TECHNIQUES FOR HYDROCARBON AND ORGANIC SOLVENT EMISSIONS FROM STATIONARY SOURCES

NATO Committee on the Challenges of Modern Society

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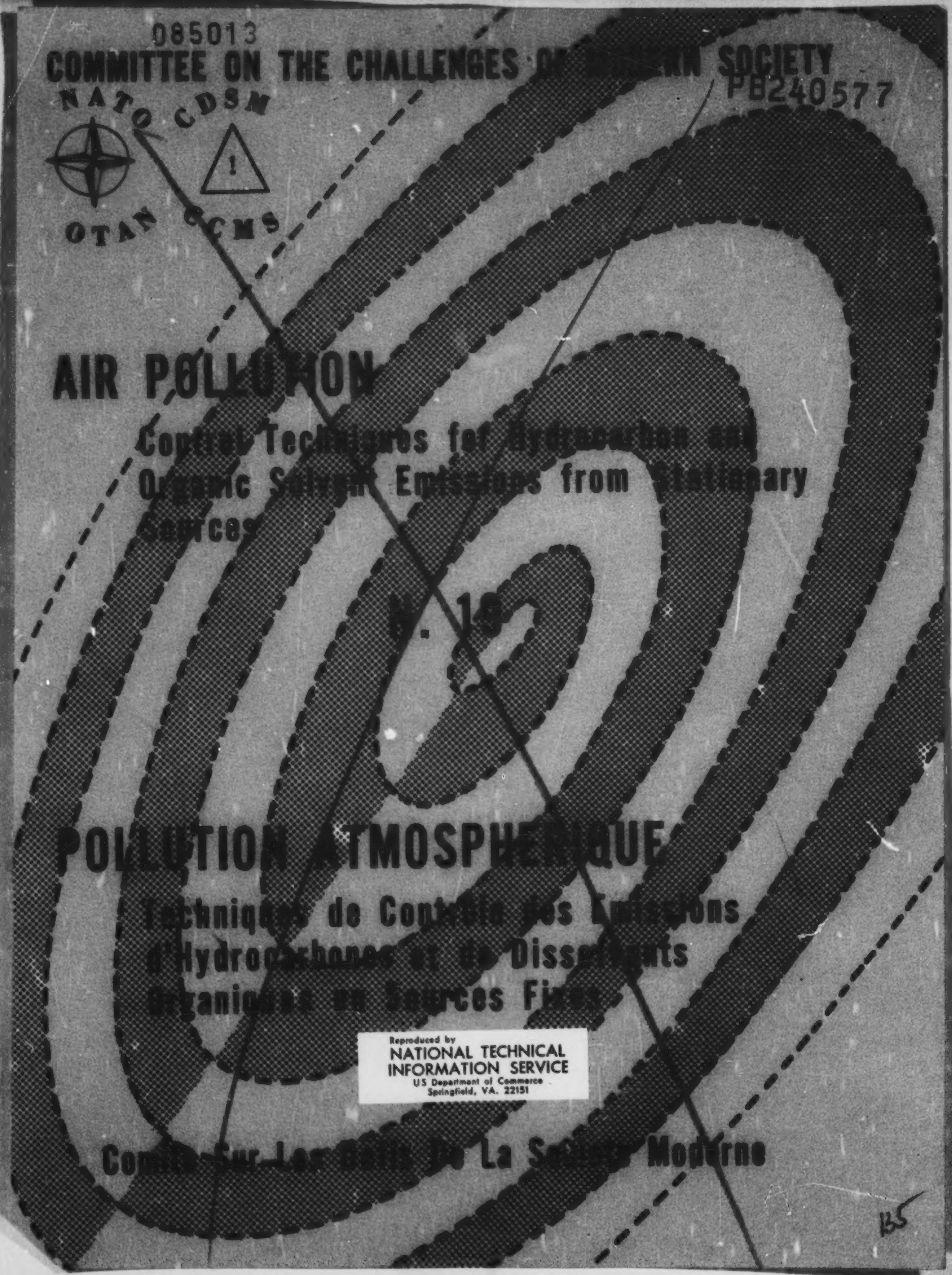

AIR POLLUTION

Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources

N. 19

POLLUTION ATMOSPHERIQUE

Techniques de Contrôle des Emissions d'Hydrocarbones et de Dissolvants Organiques en Sources Fixes

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CONTROL TECHNIQUES
FOR
HYDROCARBON AND ORGANIC SOLVENT EMISSIONS FROM STATIONARY SOURCES

RTI

PREPARED FOR
THE COMMITTEE ON THE CHALLENGES
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October, 1973

OTHER NATO/CCMS AIR POLLUTION PUBLICATIONS

Technical Report of the Conference on Low Pollution Power Systems Development, N.4

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Air Quality Criteria for Particulate Matter, N.8*

Air Quality Criteria for Carbon Monoxide, N.10*

Control Techniques for Sulfur Oxide Air Pollutants, N.12**

Control Techniques for Particulate Air Pollutants, N.13**

Proceedings of the Third Meeting of the Expert Panel on Air Pollution Modeling, N.14

Air Quality Criteria for Nitrogen Oxides, N.15**

Control Techniques for Carbon Monoxide Emissions from Stationary Sources, N.18**

Control Techniques for Nitrogen Oxide Emissions from Stationary Sources, N.20**

Proceedings of the Fourth Meeting of the Expert Panel on Air Pollution Modeling, N.30

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FOREWORD

This document is a compilation of information on methods for the control of hydrocarbon and organic solvent emissions that was assembled by the Expert Panel for Air Pollution Control Technology, The Committee on the Challenges of Modern Society, NATO, for distribution to the member countries.

The Chairman of the Expert Panel wishes to acknowledge the efforts of scientists from the pilot countries, scientists from observer countries, and the many other persons who assisted in the preparation of this document and the four companion volumes: Control Techniques for Particulate Air Pollutants, Control Techniques for Carbon Monoxide Emissions from Stationary Sources, Control Techniques for Sulfur Oxide Air Pollutants, and Control Techniques for Nitrogen Oxide Emissions from Stationary Sources.

Thanks are due the Environmental Protection Agency of the United States for permission to use their document, Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources, which was published in 1970, as a basis for this effort. Representatives from this agency deserve special recognition.

Major contributions were made by a team of scientists from the Federal Republic of Germany under the direction of Dr. Dieter Hartmann. These contributions were invaluable to the success of the effort.

Recognition should also be given to the team from the Research Triangle Institute, Research Triangle Park, North Carolina, USA, for their efforts in literature searches, writing, and editorial work.

Lastly, acknowledgment should be given to those secretaries and other support personnel who have made the panel effort possible.

John K. Burchard, Ph.D.
Panel Chairman

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SUMMARY

Hydrocarbons and organic solvents found in ambient air originate from both stationary and mobile sources. In 1970, an estimated 31.7 Gkg of hydrocarbons were emitted in the United States. Of the sources surveyed, motor vehicles were the largest single emitters of HC, accounting for 17.7 Gkg, or 56 percent of the total. Industrial process losses were the next largest source, accounting for 5.0 Gkg. Other sources, such as forest fires, organic solvent evaporation, fuel combustion in stationary sources, and disposal of solid wastes accounted for the remaining emissions.

HYDROCARBON AND ORGANIC SOLVENT SOURCES

Internal Combustion Engines

Hydrocarbons are emitted for the exhaust, crankcase, and from evaporation losses. An estimated 17.7 Gkg of hydrocarbons were emitted by gasoline and diesel power vehicles in 1970. All gasoline-powered motor vehicles accounted for approximately 99 percent, while automobiles accounted for 74 percent of the total. Urban driving represented about 50 percent of the total travel; however, almost 59 percent of the HC emissions took place in the urban areas.

Stationary Combustion Sources

HC emissions from stationary combustion sources were an estimated 0.54 Gkg per year in 1970. Half of this total is estimated to arise from the use of natural gas, while the balance comes predominantly from coal and fuel oil. Kerosene and wood are minor sources making up the combined total.

Industrial Sources

Industrial processes account for an estimated 5.0 Gkg per year of HC emissions. These processes include petroleum refining, chemical manufacturing, gasoline distribution and marketing, coal coking, fuel burning, waste disposal, and food processing. Organic solvent emissions originate from manufacture and application of protective coatings, manufacture of rubber and plastic products, degreasing and cleaning of metal parts, and printing.

Solid Waste Disposal

Solid waste disposal resulted in estimated emissions of 1.8 Gkg of hydrocarbons and organic solvents in 1970.

CONTROL METHODS

Methods used to control hydrocarbon and organic solvent emissions from stationary sources may be broadly categorized as follows: operation or process changes, substitution of materials, and installation of control equipment. The techniques used for control are: incineration, adsorption, absorption, and condensation.

Incineration devices employ three methods: thermal incineration, catalytic incineration, and direct flame afterburning.

Adsorption involves the collection of the vapors in the capillary surfaces of an adsorbent medium. After the medium has adsorbed an optimum amount of the material, the gas stream is stopped and the adosrbent bed is regenerated.

Absorption is the transfer of a soluble component from a gas phase into a relatively nonvolatile liquid absorbent. Common absorbents are water, mineral oil, nonvolatile hydrocarbons, and aqueous solutions such as oxidizing agents or alkalies. Contact between gas and liquid is provided in bubble plate columns, packed towers, jet scrubbers, spray towers, and venturi scrubbers.

Condensers collect organic emissions by lowering the temperature of the gaseous stream to the condensation point of that material. Condensers are of two types: contact and surface. In contact condensers the gaseous stream is brought into direct contact with the cooling liquid, the condensed material mixing with the coolant. In a surface condenser the vapors to be condensed and the cooling fluid are separated by a metal wall.

EMISSION FACTORS

Emission factors may be used to estimate emissions from sources for which accurate test results are unavailable. Process emission factors for some selected source types are presented in Chapter 5.

1. INTRODUCTION

Hydrocarbons and other organic matter in the atmosphere are known to have many adverse effects upon health and welfare, and reduction of emissions of these pollutants is of prime importance to any effective air pollution abatement program. This document has been prepared to summarize current information on organic air pollutants--sources and methods of control.

Hydrocarbons and organic pollutants originate from a variety of sources, and the emissions vary widely in physical and chemical characteristics. The many agricultural, commercial, domestic, industrial, and municipal sources of these air pollutants are described individually in this document. The nature and quantities of the emissions from the various processes are discussed, and methods of control that have been successfully applied are listed.

The control techniques described herein represent a broad spectrum of information from many engineering and other technical fields. The devices, methods, and principles have been developed and used over many years, and much experience has been gained in their application. They are the techniques generally applicable to the broad range of organic emission control problems.

A tabulation of emission factors from which overall emissions for the various sources can be estimated is presented. Although the factors are normally for sources with no control, where applicable, emission factors are given for representative types of control.

When reference to"BRD" is made, the initials stand for Bundes Republik Deutschland (Federal German Republic).

2. BACKGROUND INFORMATION

2.1 DEFINITIONS

Hydrocarbons are organic compounds containing hydrogen and carbon. Organic solvents may contain, in addition to hydrogen and carbon, one or more of the following elements: oxygen, nitrogen, sulfur, and halogens. In this document the term "organic solvent" includes diluents and thinners, which contain such compounds as ketones, aldehydes, amines, chlorinated hydrocarbons, and sulfides. A discussion of the nomenclature of these organic compounds is beyond the scope of this work; the reader may find this information in a reference book.[1]

The major divisions of hydrocarbons are (1) aromatic, (2) aliphatic, and (3) alicyclic. If the molecule has a benzene structure (a six-carbon ring containing three double bonds), it is aromatic; if no ring structure exists, it is aliphatic; and if a ring other than the benzene ring is present, it is alicyclic. Aliphatics include saturated paraffins (C_nH_{2n+2}) and unsaturated alkenes (C_nH_{2n}) and alkynes (C_nH_{2n-2}). Alkenes, better known as olefins (C_nH_{2n}), are generally the most reactive of the organic compounds in photochemical smog formation, although reactivity varies widely with chemical structure. Many other gaseous organic compounds that are reactive in the atmosphere in the presence of sunlight undergo chemical and physical reactions that produce other substances with greatly altered environmental impact. Such photochemical reactions are of prime importance in air pollution control; reaction products and their atmospheric effects are discussed elsewhere.

2.2 MAJOR SOURCES

Atmospheric hydrocarbons and other organic compounds have four origins: petroleum, coal, natural gas, and biological products. Organic gases can escape to the atmosphere at many points during the production, processing, storage, transport, and ultimate use of the originating organic material.

Potential sources of hydrocarbon emissions in petroleum production and product processing include leakage from oil field operations, refining, gasoline storage tanks, gasoline-loading facilities, blowing of asphalt, blowdown systems, catalyst regenerators, processing vessels, flares, compressors, pumps, vacuum jets, waste-effluent handling equipment, and turnaround operations.

Gasoline distribution and marketing systems emit hydrocarbon vapors from tank-truck loading racks, service station tank-filling operations, and automobile tank-filling operations.

Organic solvents are derived mainly but not exclusively from petroleum. They are used in many kinds of operations. Chemical, drug, and pharmaceutical manufacturing plants can be sources of organic emissions from those operations involving the use of organic solvents. Rubber and plastic product manufacturing often involves the use of organic-solvent-based-adhesives and other solvent uses that lead to organic emissions. Paint and varnishes, lacquers, undercoatings, etc., are composed of 40 to 80 percent organic solvents, which evaporate during or after the application of the coating. Degreasing and cleaning of metal items can cause significant organic emissions. Vapor-phase degreasing is the most widely used method, but spray degreasing is also used. Drycleaning of clothing utilizes organic solvents and contributes to emissions. The manufacturing processes for solvents and solvates are also potential sources.

Metallurgical coke plants emit varying amounts of hydrocarbons, depending on type of furnace, operating methods, maintenance practices, and other factors.

Fuel-burning equipment of all types can emit organics if it is not properly adjusted, not adequately maintained, or not operated correctly.

Waste disposal by burning of refuse is the greatest offender in this category. Inefficient incinerators are also significant sources. Carbonaceous material from many sources is disposed of by burning.

Miscellaneous sources of organic gases from biological sources include fermentation processes, food processing, organic fertilizer processing, wood distillation, and soap manufacturing.

An estimated 31.7 Gkg of hydrocarbons were emitted from industrial, commercial, and domestic sources in the United States during 1970.[2] Table 2-1 shows the contribution to this total from each source category. Transportation is the largest individual emitter of hydrocarbon pollution.

Table 2-1. - HYDROCARBON EMISSIONS BY SOURCE CATEGORY, 1970[1]

Source category	Quantity (Gkg)	Percent of Total
Transportation	17.69	55.9
Fuel Combustion (Stationary)	0.54	1.7
Industrial Processes	4.99	15.8
Refuse Disposal	1.81	5.7
Miscellaneous	6.62	10.9
	31.65	100.0

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1. Introduction, with Key and Discussion of the Naming of Chemical Compounds for Indexing. Chem. Abstracts Subject Index. 56 1N-98N, Jan-June 1962.

2. OAP Data File of Nationwide Emissions, 1970. National Air Data Center, Applied Technology Division, July 1972.

3. STATIONARY EMISSION SOURCES

Hydrocarbon and organic emissions from stationary sources originate primarily from industrial processes; fuel combustion sources contribute small but significant amounts. Specific sources and their emission characteristics are discussed in this section.

Currently, the best estimates for total United States hydrocarbon emissions from stationary sources (Table 3-1) are gross approximations based on emission factors and on quantities of fuels consumed, refuse burned, and raw materials processed. Hydrocarbon and organic emissions from mobile sources are discussed in another document.

Data from the Federal German Republic will be referenced as BRD (Bundes Republik Deutschland).

Table 3-1. - SUMMARY OF NATIONWIDE HYDROCARBON EMISSIONS, 1970

Source	UNITED STATES[a]		BRD	
	Mkg/yr	Percent of total	Mkg/yr	Percent of total
1. Transportation	17 800	55.8	700[c]	58.3
a. Motor vehicles	15 200	47.8	660	55.0
1. Gasoline	15 100	47.5	600	50.0
2. Diesel	90	0.3	60	5.0
b. Aircraft	370	1.1	4	0.3
c. Railroads	90	0.3	8	0.7
d. Vessels	273	0.9	14	1.3
e. Non-highway use of motor fuels	1 810	5.7	12	1.0
2. Fuel combustion in stationary sources	545	1.8	200[d]	16.7
a. Coal	181	0.6	130	10.8
b. Fuel oil	91	0.3	40	3.4
c. Natural gas	273	0.9	30	2.5
d. LPG and kerosene	0	0.0	0	0.0
e. Wood	0	0.0	0	0.0
3. Industrial processes	5 000	15.7	100[e]	8.3
4. Solid waste disposal	1 810	5.7		
5. Miscellaneous	6 620	21.0	200[f]	16.7
a. Forest fires	273	0.9		
b. Structural fires	90	0.3		
c. Coal refuse	90	0.3		
d. Agricultural burning	2 540	8.0		
e. Organic solvent evaporation	2 720	8.6		
f. Gasoline marketing[b]	910	2.9		
TOTAL	31 770	100.0	1 200	100.0

[a] Reference 1.

[b] Reference 2.

[c] Priv. calculation (emission factor 30 kg/m^3 for gasoline). References 3 and 4.

[d] Reference 5.

[e] Reference 4.

[f] Estimation.

3.1 FUEL COMBUSTION SOURCES

Incomplete combustion of fuels results in the emission of hydrocarbons and other organic material. If the combustion equipment is properly operated and designed, emissions are minimized, and control devices for hydrocarbons are not always needed.

Fuels are burned in a wide variety of equipment ranging from small hand-fired coal furnaces to large oil-, gas-, and coal-fired steam-electric generating plants. Due to variations in combustion efficiency and type of fuel, hydrocarbon emissions depend on the type of equipment. Table 3-1 presents the average hydrocarbon emissions for types of fuels and furnaces.

3.2 INDUSTRIAL SOURCES

3.2.1 Petroleum Refineries

From the production of crude oil to the marketing of finished products, the petroleum industry has the potential for emitting significant quantities of hydrocarbon gases and vapors. Crude oil is first produced from the ground; then the liquid hydrocarbons are separated from the gases, light hydrocarbon vapors, and water; finally, the crude oil is stored until it is moved to the refinery where it is converted to salable products. Since crude oil as it is produced has few uses, it is refined to obtain salable products such as gasoline, kerosene, fuel oil, petrochemical raw materials, waxes, lubricating oils, and asphalt.

The design of a refinery depends on the type of crude oil and on the final products. Refineries are most easily discussed, therefore, in terms of their function; Fig. 3-1 is a schematic diagram of a typical refining process. Processing involves four major steps: separation,

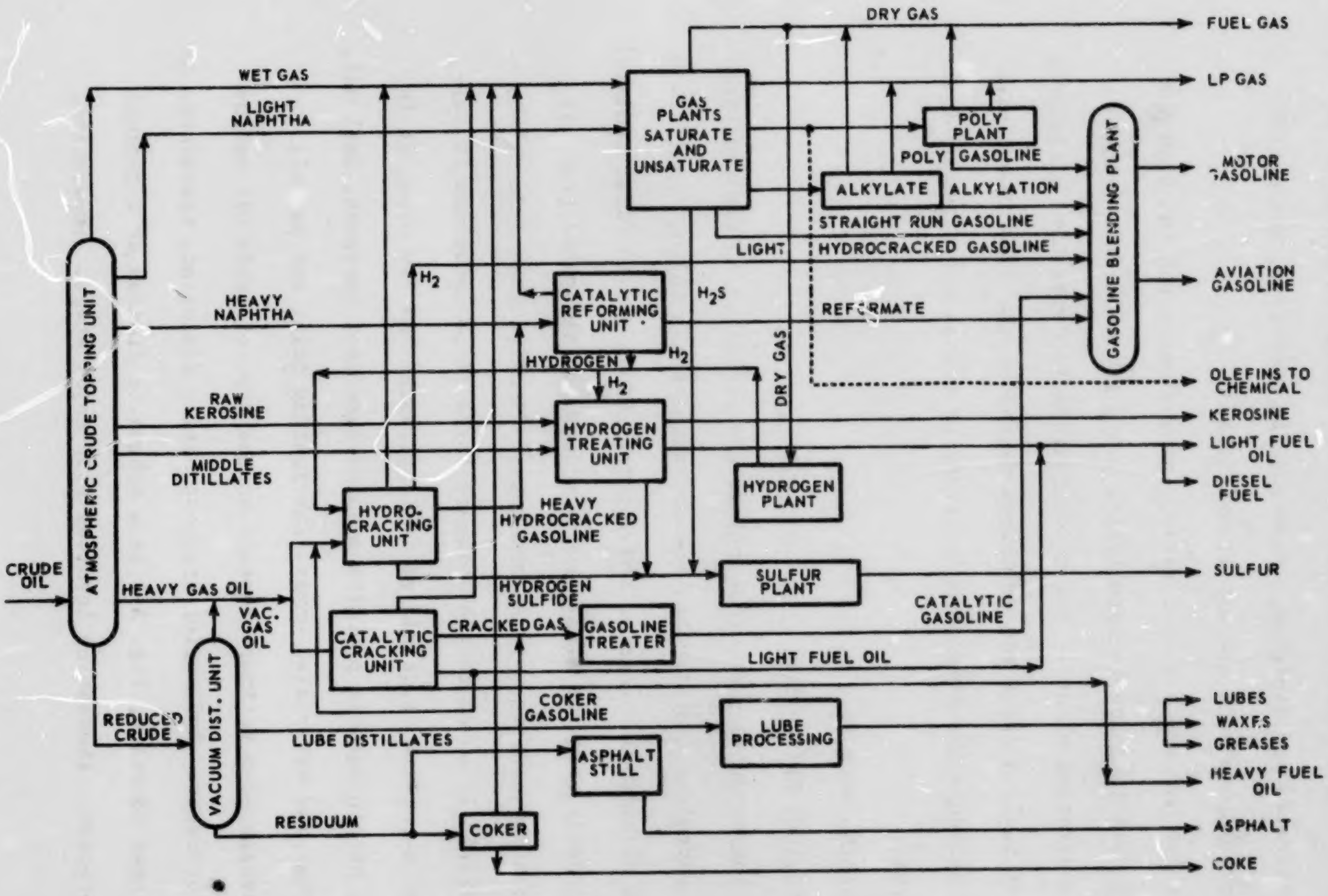
DRY GAS
FUEL GAS
WET GAS
LP GAS
LIGHT NAPHTHA
GAS PLANTS SATURATE AND UNSATURATE
POLY PLANT
POLY
GASOLINE
MOTOR GASOLINE
ALKYLATE
ALKYLATION
STRAIGHT RUN GASOLINE
LIGHT
HYDROCRACKED GASOLINE
GASOLINE BLENDING PLANT
AVIATION GASOLINE
H_2
HEAVY NAPHTHA
CATALYTIC REFORMING UNIT
H_2S
REFORMATE
ATMOSPHERIC CRUDE TOPPING UNIT
HYDROGEN
H_2
H_2
DRY GAS
OLEFINS TO CHEMICAL
RAW KEROSINE
HYDROGEN TREATING UNIT
KEROSINE
LIGHT FUEL OIL
MIDDLE DITILLATES
HYDROGEN PLANT
DIESEL FUEL
HYDRO-CRACKING UNIT
HEAVY HYDROCRACKED GASOLINE
CRUDE OIL
HEAVY GAS OIL
HYDROGEN SULFIDE
SULFUR PLANT
SULFUR
VAC. GAS OIL
CATALYTIC CRACKING UNIT
CRACKED GAS
GASOLINE TREATER
CATALYTIC GASOLINE
LIGHT FUEL OIL
VACUUM DIST. UNIT
COKER GASOLINE
LUBES
REDUCED CRUDE
LUBE DISTILLATES
LUBE PROCESSING
WAXES
GREASES
ASPHALT STILL
HEAVY FUEL OIL
RESIDUUM
COKER
ASPHALT
COKE

Fig. 3-1. Processing plan for typical complete refinery.

conversion, treatment, and blending. Separation by distillation within a specific temperature range yields fractions, the relative volumes of which are determined by the type of crude oil.

Fractions of high-molecular-weight hydrocarbons are converted into products of lower molecular weights by cracking--for example, cracking partially converts heavy gas oil to gasoline. If a catalyst is used (the more usual case), the conversion is called catalytic cracking; if not, it is thermal cracking, which requires higher temperatures and pressures. Improving the yield and quality of a gasoline fraction requires catalytic reforming: The molecules of the gasoline feedstock are rearranged and dehydrogenated to produce high-octane gasoline blending stocks. Isomerization rearranges molecules to increase the octane number; it also increases molecular branching, but it does not add to or remove anything from the original molecule. In other conversion processes, liquid gasoline is made from the hydrocarbon gases generated during cracking: Polymerization joins two or more olefin molecules, and alkylation joins an olefin with a branched chain paraffin to yield a saturated hydrocarbon.

Treatment either purifies the fraction or prevents it from reacting with an impurity. For example, during selective hydrogenation, sulfur and nitrogen impurities in the feedstocks are converted to hydrogen sulfide and ammonia, or olefins and aromatics are hydrogenated to partial or complete saturation. Three types of chemical treatments are acid, "sweetening," and solvent extraction. Petroleum fractions are treated with concentrated sulfuric acid to remove sulfur, nitrogen, and undesirable unsaturated compounds and to improve color and odor; sweetening agents--sodium plumbite (doctor), lead sulfide, hypochlorite, and copper chloride--convert mercaptans to disulfides and thus improve odors; solvent extractions either remove undesired contaminants or concentrate desired components. Physical treatments by absorption, airblowing, electrical coalescence, and filtration also remove contaminants.

Blending of base stocks, another commonplace activity at refineries, produces a wide variety of finished products.

Equipment, facilities, and processes likely to produce organic emissions in crude oil production and refining include:

1. Storage tanks.
2. Oil-water effluent systems.
3. Catalyst regenerators.
4. Pumps.
5. Asphalt stills.
6. Pipeline valves.

Most of the emissions are due to evaporation of hydrocarbon gases and vapors from storage tanks. These emissions may be precursors of photochemical smog.

3.2.1.1 Storage Tanks--Vapors can be emitted when storage tanks "breathe," when vapors are displaced during filling, and when liquids evaporate. Tanks breathe as the contents expand and contract with the heat of day and the cool of night; during expansion, air is mixed with hydrocarbon vapors and forced out of the tank. Methods have been developed to estimate and minimize these losses.[6-9]

Pressure tanks, fixed-roof tanks, floating-roof tanks, and conservation tanks provide closed storage. Pressure tanks withstand pressures exerted by their contents and are themselves a control measure. Fixed roof tanks (vertical cylinders with flat, conical, or domed roofs) often have open vents to the atmosphere. Floating-roof tanks have pan, pontoon, or double-deck roofs. Because pan-floating roofs (flat metal plates) may buckle and lose vapors or sink, pontoon sections, which often have a vapor trap on the underside, are often added to the exposed decks of large-diameter tanks to minimize the losses, and center drains are often used to handle the drainage. Double-deck roofs have compartmented dead-air space over the entire liquid surface, and the bottom deck is often coned upward to trap vapors. Conservation tanks connected to gas storage systems have internal flexible diaphragms or floating plastic blankets.

The floating section of a roof is usually about 200 mm smaller in diameter than the tank wall, and the space between is usually sealed by vertical shoes (metal plates) connected by braces to the roof. The shoes, suspended so that they exert force against the tank wall, are fixed to the roof with a fabric seal which extends from the top of the sealing plates to the inner surface of the tank and is flexible to permit it to seal even riveted areas. A secondary seal can be used as a wiper blade.

BRD practice is to blanket liquid surfaces with inert gases in storage tanks for volatile and flammable fluids.

3.2.1.2 Oil-Water Effluent Systems--A typical wastewater system for a modern refinery usually includes gathering lines, drain seals, junction boxes, and pipes of vitrified clay or concrete for transmitting wastewater from processing units to large basins or ponds used as oil-water separators. These basins, sized to receive all effluent liquid wastes from pump glands, accumulators, spills, cleanouts, sampling lines, and relief valves, sometimes even rain runoff, are earthen pits, concrete-lined basins, and steel tanks.

Organic compounds can escape from openings in the sewer system, channels, vessels, and oil-water separators. The large exposed surface area of separators can result in high levels of hydrocarbon emissions.

3.2.1.3 Catalyst Regenerators--Petroleum fractions are cracked to produce compounds of lower molecular weight by continuously circulating the catalysts in the form of powders or beads from the reactor to the regenerator. As the catalytic particles become coated with carbon and high-molecular-weight compounds, these materials are burned off in a controlled amount of air in the regenerator to maintain catalyst activity. This causes the formation of carbon monoxide and hydrocarbons. These emissions can be controlled by incineration in waste heat boilers, commonly referred to as carbon monoxide boilers.[10]

Waste heat boilers also accomplish particulate separation as well as SO_2 scrubbing.

3.2.1.4 Pumps--Pumps are used in every phase of the petroleum industry. Leakage from pumps can cause emissions wherever organic liquids are handled. The opening in the cylinder or fluid end through which the connecting rod actuates the piston is the major potential source of emissions from a reciprocating pump. In centrifugal pumps, the usual source of leakage is the point at which the drive-shaft passes through the impeller casing.

3.2.1.5 Asphalt Stills--Asphalt, normally obtained from select crude oils by means of vacuum distillation or solvent extraction, is sometimes reacted with air to make it suitable for paving, roofing, or pipe coating. Air-blowing is mainly a dehydrogenation process: Oxygen in t[illegible] air combines with hydrogen in the oil molecules to form water vapor. The loss of hydrogen results in polymerization or condensation of the asphalt to the desired consistency.

Blowing, usually carried out in asphalt batches, starts at 420 to 480 K and needs little additional heat since the reaction becomes exothermic. Effluents from the air-blowing stills include oxygen, nitrogen, water vapor, sulfur compounds, and hydrocarbon gases, odors, and aerosols. Bitumen, normally obtained from crude oils, generates losses of organic components in storage, distribution, mixing, and in the downstream processing operations (manufacture of tar paper and insulating materials).

3.2.1.6 Pipeline Valves--Valves are used in every phase of the petroleum industry where petroleum or petroleum products are transferred by piping from one point to another. Manual and automatic valves used to regulate the flow of fluids are subject to leakage from the valve stem as a result of vibration, heat, pressure, and corrosion or improper maintenance of valve-stem packing.

3.2.2 Gasoline Distribution Systems

Gasoline and other petroleum products are distributed from the refinery to the consumer by pipelines, trucks and trailers, railroad tankcars, and ocean-going tankers, as shown in Fig. 3-2. Intermediate storage and loading stations that receive products from refineries by pipeline or tanker are called terminals; those supplied by trucks and

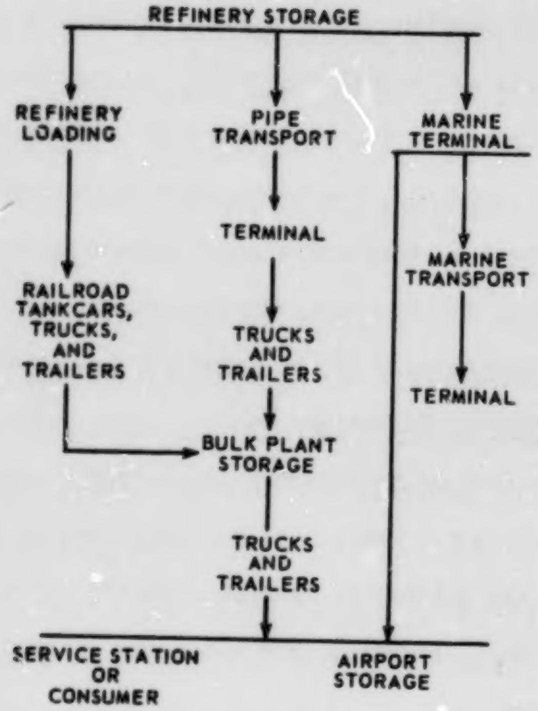
REFINERY STORAGE
REFINERY LOADING
PIPE TRANSPORT
MARINE TERMINAL
TERMINAL
MARINE TRANSPORT
RAILROAD TANKCARS, TRUCKS, AND TRAILERS
TRUCKS AND TRAILERS
TERMINAL
BULK PLANT STORAGE
TRUCKS AND TRAILERS
SERVICE STATION OR CONSUMER
AIRPORT STORAGE

Fig. 3-2. Representation of gasoline distribution system, showing flow of gasoline and other petroleum products from refinery to consumer.

trailers are called bulk plants; marine terminals adjacent to docks are for storage of petroleum products waiting to be loaded into ocean-going tankers. From bulk storage, petroleum products are loaded into trucks, trailers, and tankcars by means of loading racks which have equipment for metering the products to be delivered.

When a tank truck or tanker is filled through an open overhead hatch or a bottom connection, the incoming liquid displaces the contained vapors, usually air and hydrocarbons, and forces them into the atmosphere. Ordinarily, when gasoline is loaded, the concentration of hydrocarbons is 30 to 50 percent by volume. Table 3-2 shows a typical analysis of the vapors emitted during the overhead loading of motor gasoline into tank vehicles.[11]

The volume, as well as composition, of vapors emitted during loading is greatly influenced by the type of loading or filling.[11] Overhead loading, presently the most widely used, includes splash and submerged filling: In splash filling, the outlet of the delivery tube is above the liquid surface during all or most of the loading; in submerged filling, the outlet is extended to within 150 mm of the bottom and is submerged beneath the liquid during most of the loading. Splash filling generates more turbulence and therefore more hydrocarbon vapors than submerged filling. Bottom loading is accomplished by connecting a swing-type loading arm or hose at ground level to a matching fitting on the underside of the tank vehicles (Fig. 3-3) so all the loading is submerged, turbulence is minimized, and less vapor is produced. Loading and unloading operations are the primary sources of emissions in the distribution of gasoline and petroleum products.

Table 3-2. - TYPICAL ANALYSIS OF VAPORS FROM LOADING OF GASOLINE INTO TANK TRUCKS

Fraction	Volume, percent	Weight, percent
Air	58.1	37.6
Hydrocarbon:	41.9	62.4
Propane	0.6	0.6
Isobutane	2.9	3.8
Butene	3.2	4.0
N-butane	17.4	22.5
Isopentene	7.7	12.4
Pentene	5.1	8.0
N-pentane	2.0	3.1
Hexane	3.0	8.0

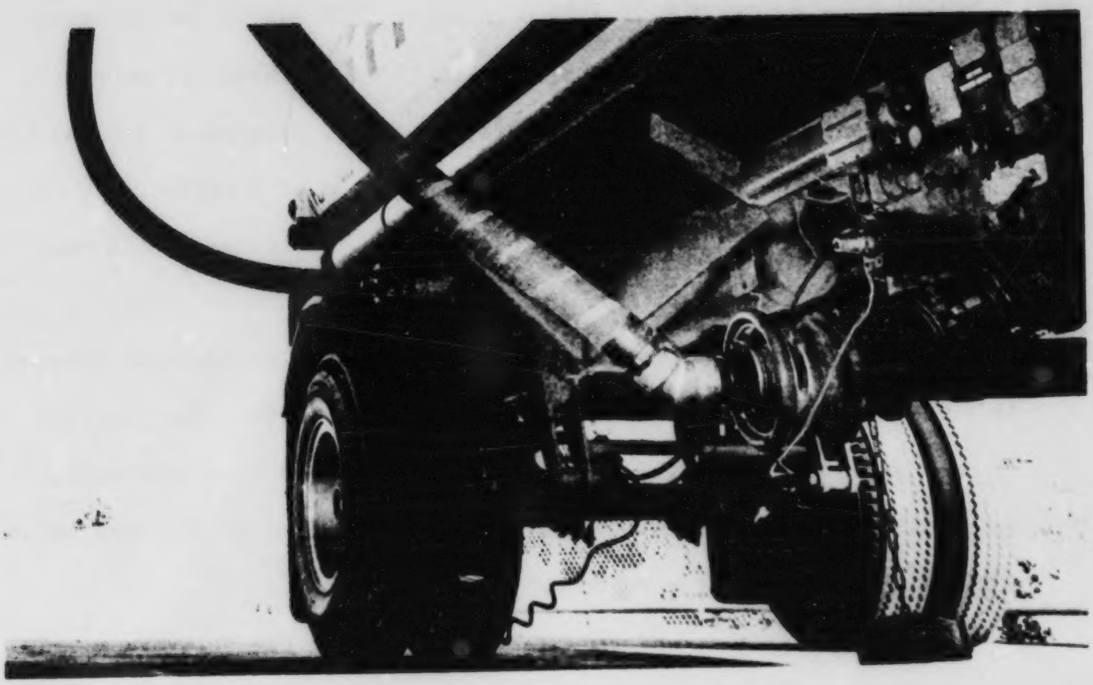

Fig. 3-3. View of bottom-loading station.

These transfer operations point up the urgent need for universally adopted standards in types and sizes of connectors.

3.2.3 Chemical Plants

Manufacturers of synthetic organic chemicals such as elastomers, dyes, flavors, perfumes, plastics, resins, plasticizers, pigments, pesticides, rubber processing materials, and miscellaneous solvents have the problems of controlling emissions of hydrocarbons from raw materials and from products made from these materials.

According to the U.S. Tariff Commission, 106 Gkg of raw materials were consumed by the chemical industry in 1970.[12] These raw materials were obtained from coal (coke oven gas, coal tar, water-gas, and oil-gas tar) and from petroleum. The quantities of the most important raw materials--benzene, toluene, xylene, naphthalene, and creosote oil--are shown in Table 3-3.

The crude products produced from petroleum and natural gas totaled 35.3 Gkg in 1970, an increase of 9.2 percent over 1969. The quantity of each product is itemized in Table 3-3; from these crude products, synthetic organic chemicals were produced as itemized in the same table. Comparable BRD production is shown in Table 3-4.

Pipelines, barges, and ships, by facilitating the delivery of raw materials and products, have stimulated the growth and geographic spread of petrochemical manufacturing. Organic chemicals, or petrochemicals, are manufactured by largely conversion processes which involve continuous processing in large volume and automated control by instrumentation (i.e., by computers). Generally, the type of emission is identified by the type of raw material and auxiliary raw material and by the type of conversion.

Table 3-3. - QUANTITIES OF RAW MATERIALS AND INTERMEDIATE PRODUCTS CONVERTED TO SYNTHETIC ORGANIC CHEMICALS, UNITED STATES, 1970[12]

(Mkg)

		Coal[a]	Petroleum	Total
RAW MATERIALS PRODUCED FROM COAL AND PETROLEUM				
1.	Benzene	311.5	3 540	3 851
2.	Toluene	55.8	2 650	2 706
3.	Xylene	14.73	1 745	1 760
4.	Naphthalene	194	--	194
5.	Creosote oil	516	--	516
		1 092	7 935	9 027
CRUDE PRODUCTS FROM NATURAL GAS AND PETROLEUM				
1.	Aromatics, and naphthenes[b]			
	a. Benzene			3 480
	b. Naphthalene			131.6
	c. Napthenic acid			11.2
	d. Toluene			2 680
	e. Xylene, mixed, total			1 745
	f. All other aromatics and naphthenes[c]			1 513
				9 561
2.	Aliphatic hydrocarbons			
	a. C_2 hydrocarbons: acetylene			214
	ethane			2 250
	ethylene			8 200
	b. C_2 and C_3 hydrocarbons, mixed			960
	c. C_3 hydrocarbons: propane			3 970
	propylene			3 000
	d. C_4 hydrocarbons			4 320
	e. C_5 hydrocarbons			494
	f. All other aliphatics and derivatives			1 965
				25 373

Table 3-3. - QUANTITIES OF RAW MATERIALS AND INTERMEDIATE PRODUCTS CONVERTED TO SYNTHETIC ORGANIC CHEMICALS, UNITED STATES, 1970—Continued

(Mkg)

3. Synthetic organic chemicals produced	
a. Miscellaneous chemicals and solvents	31 900
b. Dyes	106.3
c. Elastomers	2 010
d. Flavor and perfume materials	45.4
e. Pesticides and related products	469
f. Pigments	25.8
g. Plasticizers	606
h. Plastics and resins	8 710
i. Rubber processing chemicals	135
	44 007.5

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[a] U. S. Tariff Commission figures for coke oven gas, coal, water-gas, and oil-gas tar.

[b] Chemical raw materials designated as aromatics are sometimes identical to those obtained from the distillation of coal tar; statistics in the the table are for materials derived from petroleum and natural gas. Statistics on production or sales of benzene, xylene, and naphthalene from all sources are given under "Tar and Tar Crudes."

[c] Includes data for 90-percent benzene, crude cresylic acid, alkyl aromatics, distillates, solvents, and miscellaneous cyclic hydrocarbons.

Table 3-4. - QUANTITIES OF RAW MATERIALS AND INTERMEDIATE PRODUCTS CONVERTED TO SYNTHETIC ORGANIC CHEMICALS IN THE BRD, 1970

(Mkg)

RAW MATERIALS PRODUCED FROM COAL AND PETROLEUM	
Aromatics and naphthenes	
Benzene	850
Naphthalene	150
Toluene	188
Xylenes, mixed, total	220
All other aromatics and naphthenes	779
Acyclic hydrocarbons	
Acetylene	300
Ethylene	2 000
Propylene	800
Butadiene, butylene	500

SYNTHETIC ORGANIC CHEMICALS PRODUCED	
Paints	1 000
Flavor and perfume materials	150
Pesticides and related products	170
Pigments	800
Plasticizers	250
Plastics and resins	3 600

Of the thousands of chemical manufacturing processes, each has unique control problems. The types of conversions used in these processes are classified below.

Alkylation is the union of an olefin with an aromatic or paraffinic hydrocarbon. Ethyl benzene is produced by alkylating benzene with ethylene.[13] Naphthalene is produced by dealkylation of a petroleum fraction.[14]

Amination forms an amino compound either by using ammonia (or a substituted ammonia) as the agent or by reducing a nitro compound. Ethanolamines, for example, are obtained when ethylene oxide is bubbled through an ammonia solution.

Hydrogenation, the addition of hydrogen, is used to manufacture a broad range of products. For example, methanol is made by reacting carbon monoxide with hydrogen. Dehydrogenation, the removal of hydrogen, produces unsaturated compounds; benzene is made by dehydrogenation of substituted cyclohexanes.

Dehydration, the removal of water, produces ethers from alcohols; and hydration, the addition of water, produces ethyl alcohol from ethylene.

In esterification, an alcohol reacts with an organic acid to form an ester. Ethyl alcohol reacts with acetic acid to form ethyl acetate, an important solvent.

Halogenation and dehalogenation are the addition or removal of a halogen--chlorine, bromine, iodine, or fluorine. Methyl chloride is made by chlorination of methane.

Oxidation, the addition of oxygen, is one of the most valuable conversion processes. Ethylene oxide is made by oxidation of ethylene. The cheapest oxidizing agent is air, but pure oxygen has advantages in many applications.

Nitration introduces nitrogen into hydrocarbons. Nitrobenzene is an important product of nitration.

Polymerization is the reaction of simple molecules to form more complex polymers--for example, ethylene is polymerized to polyethylene.

In any chemical conversion, the potential sources of emissions are the raw materials and the products, and chemical reactions for production of a desired product usually result in several byproducts. Although the formation of byproducts is minimized by adjusting the conversion conditions, the quantities formed must either be recovered for use or be properly disposed of as wastes.

The major sources of emissions are streams of waste gases, vapors from distillation columns, and leakage from feed and product transport lines. Plants that generate their own steam for refining and for power have emissions characteristic of power plants as an inherent part of the total. Plants that manufacture or regenerate catalysts usually emit nonhydrocarbons. Plants that produce their own crude products have emissions similar to those from petroleum plants. Annual total emissions were estimated for an ethylene plant producing 230 Mkg/yr. Emission factors, taken from Public Health Service Publication No. 763,[15] were used for individual pieces of equipment to derive the results shown in Table 3-5; for these estimates, all pumps, compressors, valves, etc., were counted; and the composition of the process streams was delineated.

Table 3-5. - CALCULATION OF HYDROCARBON LOSSES FROM PROCESS EQUIPMENT IN 230 Mkg/yr ETHYLENE PLANT[15]

Emission source	Loss factor[a]	Number or capacity	Emissions, kg/day
Valves	0.068 kg/day-valve	4 500 valves × 0.068	304
Pumps (mech. seal)	1.45 kg/day-seal	150 pumps × 1.45	218
Compressors (centrifugal, mechanical seal)	1.45 kg/day-seal	10 comp. × 2 seals × 1.45	29
Compressors (reciprocating packed seal)	2.44 kg/day-seal	1 comp. × 2.44	2.44
Cooling water	0.72 kg/1 000 m^3	$\frac{189\ m^3/min \times 60 \times 24}{1\ 000} \times 0.72$	196
Process drains and waste-water separators	0.426 kg/m^3 cap.	3 200 m^3 × 0.426	1 365
Blowdown systems	0.283 kg/m^3 cap.	3 200 m^3 × 0.283	905
Relief valves (operating vessels)	1.31 kg/day-valve	400 valves × 1.31	524
Relief valves (storage tanks)	0.271 kg/day-valve	14 tanks × 2 valves × 0.271	7.6
Storage tanks (floating roof)(VP < 10.4 kN/m^2)	0.0136 kg/day/m^3 cap.	80 000 m^3 × 0.0136	1 090
Storage tanks (floating roof)(VP > 10.4 kN/m^2)	0.0048 kg/day/m^3 cap.	800 m^3 × 0.0048	3.8
Miscellaneous losses	0.0283 kg/day/m^3 cap.	3 200 m^3 × 0.0283	90

Total hydrocarbon emission (calculated) = 4 735 kg/day

Loss on plant feed,[b] $\frac{4\ 735\ kg}{3\ 200\ m^3 \times 705\ kg/m^3}$ = 0.21 weight percent

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[a] These loss factors are applicable to plants practicing extensive hydrocarbon control.

[b] The range of emissions from hydrocarbon processing plants may range from 0.1 to 0.6 percent by weight of plant throughput. The lower value calculated here is applicable to an area such as Los Angeles County where stringent control is practiced.

3.2.4 Paint, Lacquer, and Varnish Manufacture

Paint, lacquer, and varnish coatings for decorative and protective purposes and, in some instances, for electrical insulation and chemical resistance are the products of precisely controlled chemical reactions and accurately proportioned formulations, which may include natural or synthetic drying oils, pigments, volatile solvents, resins, driers, thinners, plasticizers, and antioxidants.[16] Coatings may be divided into two types: pigmented or nonpigmented. The vehicle (or binder) is common to both types. Most of the materials, other than pigments, are organic with varying degrees of volatility; thus handling, mixing, and processing produce different amounts of atmospheric pollution depending on the raw materials, the combinations of these materials, and the conditions to which they are subjected.[16]

Producing the vehicle for paint or varnish by either chemical reactions and/or cooking processes vaporizes part of the ingredients. Other losses are from volatile solvents and thinners used to produce proper consistency for the finished product and from the handling and storage of raw materials and intermediate products.[16] Even with these losses, more hydrocarbons usually are emitted from the application of coatings (Section 3.3.6) than from the manufacturing processes. Production of varnish appears to be the largest contributor of hydrocarbon emissions and thus will be discussed in considerably more detail than paint and lacquer production.

3.2.4.1 Paint Manufacturing--Paint can be defined as a pigmented liquid that converts to a relatively opaque solid film after application.[17] Enamels are paints which form an especially smooth, glossy film.

Paint manufacturing consists of the following operations:

1. Mixing pigment with sufficient vehicle to make a paste of proper grinding consistency.
2. Grinding the paste on a mill until aggregates are broken down.
3. Letting down (diluting) the ground paste with the remaining materials.
4. Tinting to required color.
5. Testing.
6. Straining, filling, and packaging.

Paint manufacturing is still largely a batch process because of the large number of raw materials and finished products required, many of which must be custom formulated and processed.[18]

A small amount of pigment fines is emitted from mixing; solvent loss generally amounts to no more than 1 to 2 percent of the solvent used.[16] The two sources of hydrocarbon emissions are grinding, during which the batch may heat up considerably and lead to vaporization of certain ingredients, and thinning, during which vaporization of solvents occurs. Thinning premixed paint pastes to the required consistency for application involves dilution with volatile aliphatic or aromatic hydrocarbons, alcohols, ketones, esters, and other highly volatile materials.[16] A recent estimate of paint manufacture is that about 0.5 percent of the weight of the paint is emitted as hydrocarbons.

3.2.4.2 Lacquer Manufacturing--Lacquers, solutions of resins in organic solvents, harden as a result of evaporation of the solvent rather than oxidation or polymerization.[18] Pigmented laquers, called lacquer enamel or pigmented lacquer, are more resistant to weather than are clear lacquers. Nitrocellulose, the basic film-forming ingredient in lacquer, is made from cotton linters, the short fibers remaining on cotton seeds after the long fibers have been removed by gins.[19] The fibers are purified by boiling in caustic solution until they become pure white and then nitrated to produce nitrocellulose, which is blended with resins, plasticizers, volatile solvents, and diluents to produce properties such as elasticity, surface adhesion, film depth or body, luster, and drying characteristics. For pigmented lacquers, a separate grinding or milling step is required.

Resins used in lacquers must be soluble in mixtures of esters, alcohols, and hydrocarbons. Usually, blends of several solvents are required to provide the proper consistency for application. Some of the resins used are shellac, elimi, dammar, ester gum, and alkyds.[19] The solid ingredients, as well as the method of application, dictate the selection of solvents. Solvents used in lacquer manufacture are mainly esters, ketones, etc.; the latent solvents are ethyl, butyl, and amyl alcohols; the diluents are petroleum thinners and coal tar solvents.[19]

Hydrocarbon emissions from lacquer manufacture consist of vaporized solvents and diluents, but unless temperatures become elevated, the losses are small.

3.2.4.3 Varnish Manufacturing--Varnish has been defined in various ways by technical societies and several authors.[11,17,19] Some authorities say varnish is a colloid; others say it is a solution. The one common definition is that varnish is unpigmented; consists of resins, oils, thinners; and dries by evaporation of the solvents and by oxidation and polymerization of the remaining constituents.

The most common varnishes are the oleoresinous ones: oil-plus-resin, oil, and oil-modified solutions of one or more (natural or synthetic) resins in a drying oil and a volatile solvent. All oleoresinous varnishes dry by oxidation or by oxidation and condensation or by oxidation, condensation, and polymerization.[19] The next most common type, for which shellac is an example, is spirit varnish, which consists of alcohol solvents plus either natural or synthetic resins but little or no oil. This type dries either by evaporation or by evaporation and some polymerization. Other types developed recently include alkyd resin varnish, which is a solution of alkyd resin (a synthetic polyester co-reacted with a vegetable oil) in a volatile solvent with added drier; asphalt varnish, which is a solution of asphalt in a volatile solvent; and lithograph varnish, which is used as a vehicle in printing ink.

Varnish manufacturing includes cooking, thinning, mixing, filtering, storing and aging (if necessary), testing, and packaging. The most important step is cooking. Cooking performs many functions; the most important ones are:

1. Depolymerization of resins and oils. Natural resins are insoluble in many film-forming oils (e.g., linseed, tung, and castor) in oleoresinous varnishes; thus, the resin must be heated above its softening point for decomposition and depolymerization to take place so that it is soluble and can react with oils.
2. Bodying of natural and synthetic oils.
3. Melting materials to accelerate solubility and reaction.

4. Esterification of rosin, phthalic anhydride, maleic anhydride, or tall oil with a polyhydric alcohol such as glycerol or pentaerythritol.
5. Isomerization to eliminate extreme reactivity in some oils during oxidation.
6. Preparation of alkyd resins.
7. Distillation and evaporation to remove undesirable constituents such as volatiles in resins.

The above operations differ with the particular batch being cooked.

Cooking temperatures in varnish kettles range from 270 to 590 K and are usually maintained for several hours. The average batch starts to give off vapors at about 450 K; the rate of vaporization increases as the temperature increases and reaches its maximum at, or shortly after, the maximum processing temperature is reached.[16,19] Vapor emission continues as long as heating continues, but slowly decreases after the maximum is reached.

There are two types of kettles used for cooking varnish: the open kettle, which is heated over an open flame, and the newer totally enclosed kettle, which is set over or within a totally enclosed source of heat. Naturally, the open kettle allows vaporized material to be emitted to the atmosphere unless hooding and ventilation systems are provided.

Vapors emitted from varnish kettles are (1) low-melting-temperature constituents of natural gums, synthetic acids, and rosins, some of which are purposely driven off; (2) thermal decomposition and oxidation products volatilized during bodying of oils; and (3) volatile thinners distilled off during thinning of varnish.[19]

The compositions of vapors are functions of the raw materials, the cooking formulas, and the heating cycles. The raw materials include (1) oils such as linseed, castor, fish, tall, soya, tung, oiticica, and perilla; (2) resins such as phenolics, rosin, copal, dammar, manila and East India, alkyd, ester gum, acrylates, silicones, epoxies, and polyurethanes; (3) solvents and thinners such as turpentine, xylol, toluol, alcohols, aromatic and aliphatic naphthas, and dipentine; and (4) dryers such as resinates, tallates, linoleates, carbon monoxide, and manganese, lead, and zinc naphthenates.

Major constituents of the emissions from varnish kettles are fatty acids and aldehydes mixed with water vapor, acrolein, glycerol, acetic acid, formic acid, and complex residues of thermal decomposition.[19] The most unpleasant is acrolein because of its pungent, disagreeable odor, very low odor threshold, and eye-irritating characteristics. In addition, highly offensive sulfur compounds such as hydrogen sulfide, butyl mercaptan, thiophene, and allyl sulfide are emitted when tall oil is esterified with glycerine and pentaerythritol.[10]

Total emissions to the atmosphere from cooking depend on the composition of the batch, rate of temperature applications, maximum temperature of the process, method of adding solvents and driers, amount of stirring, extent of air-blowing, length of cooking time, and amount of pollution or process control equipment employed. Typical losses from various cooking processes are as follows:[16]

1. From oleoresinous varnish cooking, an average of 3 to 6 percent, with some as high as 10 to 12 percent.

2. From alkyd resin cooking, a range of 4 to 6 percent.

3. From cooking and blowing of oils, 1 to 3 percent.

4. From heat polyermization of acrylic resins, less than 1 percent.

For the process of gum-running, the amount of vapor varies from 12 to 35 percent of the original weight of copal (depending on the type of copal), the temperature, and the duration of the running process.[20] A reasonable average is a 25-percent loss.

The second largest source of emissions from varnish manufacture is thinning. Addition of solvents and thinners during cooking, which is near the boiling point of the solvents, causes large losses if the open kettle is used. Losses of solvents during thinning range from 5 to 50 percent of the total added in open thinning tanks depending on the method used and the amount of time the thinned mixture is left open.[20] However, since most manufacturers use totally enclosed tanks, the amount lost is no more than 1 to 2 percent of the solvent used.[16]

3.2.5 Rubber and Plastic Industries

The rubber and the plastic industries are analogous in that many ingredients other than the base materials are added to produce desired properties of the final products. Each ingredient is classified according to its functions, so the classification is arbitrary: (1) plasticizers or softeners, (2) vulcanizing agents, (3) accelerators, (4) activators and retarders, (5) antioxidants, (6) fillers, and (7) miscellaneous ingredients such as pigments, rubber substitutes, odorants, abrasives, stiffeners, and blowing agents.

The thermoplastics, vinyl chloride polymers and copolymers, are naturally hard but can be changed to permanently pliable materials by addition of plasticizers. The most common plasticizer is dioctyl phthalate (DOP), but sometimes diisooctyl phthalate (DIOP) is used. For flexible plastics and sponges, there are 50 or more parts of plasticizers per 100 parts of resin.

The most important operations in the manufacture of rubber are as follows: (1) physical treatment of raw rubber to prepare it for addition of compounding ingredients; (2) incorporation of various substances, especially fillers; (3) pretreatment of mix to make it satisfactory for preparing the final product; (4) formation of the final product; and (5) vulcanization or curing of the molded article. The first step in this operation is plasticization to soften the rubber. Mechanical plasticization is accomplished by rolling it on a mixing mill or internal mixer. Heat plasticization is accomplished by heating it in ovens for about 24 hours at 420 to 480 K. Chemical plasticization, accomplished by adding peptizing agents on the mills, is more rapid and economical than other means under certain conditions; typical peptizing agents are naphthyl mercaptan, xylyl mercaptan, zinc salt of pentachlorothiophenol, and dithio-bis-benzanilide.

Typical antioxidants that create hydrocarbon and organic pollutants are aromatic amines, aldehyde-amine condensation products, derivatives of secondary naphthylamines, aromatic diamine derivatives, and ketone-amine condensation products.

To vulcanize or cure the molded article, the material is held at 370 to 420 K from a few seconds to several hours. The elevated temperature volatizes the plasticizers, accelerators, and other organics and drives them off as air pollutants. One of the major problems of rubber production is odor.

3.2.6 Surface Coating Applications

Coatings applied to surfaces for protection and decoration can be broadly classified as convertible and nonconvertible.[21] Convertibles include oil paint and oil varnish coatings which dry and harden primarily through oxidation and polymerization induced by the surrounding air. Nonconvertible coatings are dissolved in volatile solvents which evaporate and leave a resin film without undergoing any significant chemical change on continued exposure.

For both classes, solvents facilitate use. The quantity of solvent purchased generally coincides with the quantity emitted; essentially all of the solvents find their way into the atmosphere. Materials referred to in the trade as diluents and thinners are included as solvents for coating applications. Most of the organic solvents in commercial or industrial uses are aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, esters, halogenated hydrocarbons, or mixtures of these. When coatings are applied, no attempt is usually made to collect emissions. However, certain coatings are amenable to control: industrial finishes requiring baking, coating coils, enameling wire, painting automobiles and other sheet metal products, and drying in lithograph ovens.

Adhesives used in making insulating materials from rock wool and glass wool are normally made from phenol/formalin resin formulations. These materials are processed through drying ovens to accelerate polymerization, thus emitting malodorous compounds. Permissible levels of these in the BRD are less than 50 $\mu kg/m^3$ for phenols and less than 10 $\mu kg/m^3$ for formaldehyde.

Inks used in printing presses contain solvents. In the case of photogravure printing, these low-boiling solvents are emitted. In offset printing machines, phenol modified rosins, dissolved in mineral oils free of aromatics, are used in the inks. These high-boiling solvents are emitted from the drying ovens which operate at 475 to 525 K.

3.2.7 Degreasing Operations

In many industrial operations, metal parts must be thoroughly cleaned with organic solvents of all grease and oil before they can be plated, painted, or further processed. Certain types of equipment operate with little or no built-in control of solvent losses; others operate with a relatively high degree of control. In general, "degreasing" implies merely the use of an organic solvent to dissolve and remove soils by any type of process. If halogenated, nonhalogenated, or mixtures of these solvents are used at or near room temperature but the equipment is not designed to control solvent losses, the process is referred to as "solvent cleaning" or "cold solvent cleaning." If an essentially nonflammable halogenated solvent of relatively high vapor density is maintained by heat input at its atmospheric boiling point and if this equipment is designed to minimize solvent losses, the process is called "vapor degreasing." In other words, vapor degreasing is a specific type of cleaning process. (Complete descriptions of solvent cleaning and vapor degreasing are in the chapter on metal cleaning in the Metals Handbook.[22])

For vapor degreasing using trichloroethylene, industrial experience indicates the following guidelines for estimating solvent vapor losses from a properly designed and operated machine:

1. Based on the open cross-sectional area of the degreaser, estimate the solvent loss as 1.2 kg (± 50 percent) for each square meter of area.
2. Based on the workload processed, estimate solvent loss as 2 to 6 dm^3/hr/1 000 kg of metal cleaned.
3. Based on the solvent turnover (boilup rate), estimate solvent loss as 1 to 2 percent of the vapor generation rate in kilograms per hour.

While emissions of solvent vapors vary from a few kilograms to as high as 600 kg/day for a single-spray degreasing booth, the total emissions from such sources in an industrialized area may be quite large.[10] It has been estimated that in Los Angeles County, degreasing vapors amounted to 85 000 kg/day in 1967.[23]

3.2.8 Drycleaning

Clothing and other textiles may be cleaned by agitating them in an organic solvent bath, rinsing with clean solvent, and drying with warm air. There are basically two types of drycleaning installations: those using petroleum solvents (Stoddard at 330 K) and those using chlorinated synthetic solvents (perchloroethylene). Because petroleum solvents are fire hazards, most zoning laws have prohibited them in residential and commercial areas and have led to development of nonflammable, chlorinated solvents. Chlorinated solvents, however, are more costly (tenfold more), more toxic, more corrosive to metals, and more deleterious to some dyes and fabrics than are petroleum solvents. Nevertheless, the trend is toward synthetic solvents for both small and large plants.[10]

Equipment for a plant using a petroleum solvent generally consists of a washer, centrifuge (extractor), tumbler, filter, and often a batch still. The centrifuge recovers solvent by spinning it from the clothes; then the clothes are dried in a warm air tumbler which is usually vented through a lint trap to the atmosphere. In synthetic solvent plants, the washer and extractor are a single unit. The closed system tumbler has a condenser for vapor recovery and is vented to the atmosphere or to a carbon adsorber only during a short deodorizing period. All cleaning plants in the BRD are now required to recover solvent vapors with activated carbon adsorbers.

In both types of plants, circulation of hot air in the tumbler leads to vaporization of the solvent and emissions to the atmosphere unless control equipment is used. Additional emissions of volatile solvents occur when storage tanks are loaded, equipment doors are opened, ductwork or equipment leaks, and solvent-soaked textiles are removed from equipment; these emissions are tolerated in petroleum plants because the low cost of the solvent gives little economic incentive for conserving the solvent during handling operations. In the petroleum plants, chemical composition of solvents is about 46 percent paraffins, 42 percent naphthenes, and 12 percent aromatic compounds. (In Los Angeles, Rule 66 led to reformulation of the solvents to reduce the aromatic content to less than 8 percent.) Based on an average per capita rate of 1.75 kg/yr,[24] total organic emissions from drycleaning are 360 Mkg/yr in the United States.

Before control measures were instituted, emissions in the BRD amounted to 24 Mkg (1967).

Emissions from synthetic plants using separate vessels for cleaning and drying are about 0.8 dm^3/kg of textiles cleaned; this drops to 0.21 to 0.29 dm^3/kg for older plants in good condition with carbon adsorbers and down to only 0.1 to 0.125 dm^3/kg of textiles for new integrated plants with activated-carbon adsorbers.[25] For plants using the same vessel for cleaning and drying, the rate is 0.4 dm^3/kg of textiles cleaned without adsorption units. Emissions from petroleum-solvent plants are about 1.25 dm^3/kg of textiles.[10] The relative tonnage is somewhat less because unit volume of synthetic solvent is about twice as heavy as a unit volume of petroleum solvent.

3.2.9 Textile Industry

Hydrocarbons are emitted during processing of synthetic fibers in the textile industry. Emulsifiers and lubricants are emitted in texturizing synthetic fibers. Dyeworks emit organic compounds from carriers which are used to dye synthetic fibers.

3.2.10 Metallurgical Coke Plants

Coke is mainly produced by the destructive distillation of coal in long rows of narrow rectangular ovens.[26] From 15 000 to 23 000 kg of coal are charged through ports in the top of the ovens, the ports are sealed, and the coking initiated by application of intense heat (1 100 to 1 500 K, almost exclusively in the United States). In about 16 to 20 hours, when the volatile matter has been driven off and carbonization is complete, the charge is pushed out into quench cars, cooled, and screened.[14] Volatile matter is ducted to equipment that extracts tar, ammonia liquor, and light oil from the gas. Approximately 35 percent of the gas (heating value, 20.5 MJ/m^3) produced during coking is recovered and used to heat the coke ovens.[27] Although the remainder of the gas is usually used to heat other nearby processes, it is sometimes flared.

In the BRD, complete control of coke oven emissions has been reported at the Essen Works by installing closed systems, steam jet evacuators, and methods of recovery.

Coke is also manufactured in beehive-type ovens. The volatile matter is not recovered; it is vented to the atmosphere. In 1970, only about 1.5 percent of the total metallurgical coke production of 60 Gkg was produced in beehive ovens.[28]

During byproduct coking, visible smoke, hydrocarbons, carbon monoxide, and other emissions originate from the following: (1) charging of coal into red-hot ovens, (2) leakage from the ovens during the coking or carbonization, (3) pushing of the charge out of the ovens, and (4) quenching of the hot coke. There are organic emissions from the last two operations due to undercoking; they decrease when measures are taken to reduce the more noticeable pollutants. At the end of the coking cycle, the oven is emptied and refilled with a new charge of pulverized coal. Since the oven interior is 1 090 to 1 250 K, volatilization of gases begins at once; and without control, these escape to the atmosphere as clouds of yellow-brown smoke. Hydrocarbons and other organic compounds are generated and emitted, but few quantitative data on organic emissions are available.

3.2.11 Sewage Treatment

Municipal sewage is treated in a primary treatment plant, an activated-sludge plant, or a trickling filter plant. All three types of plants emit organic gases, many of which are odorous. A primary treatment plant removes only solid material either by sedimentation or screening; thus hydrocarbons are emitted from the screening and grit chamber and from the settling tank. In the activated-sludge plant, the sewage, after passing through screens and a primary clarifier (settling tank), is biologically activated by compressed air; the activated sludge is settled out in a final clarifier and recycled to the aeration chamber;[29] thus volatile oils, fats, and other organic compounds are partially stripped from the liquid, as shown by the concentrations in Table 3-6, measured in the ambient air above a single plant. In a trickling filter plant, treated sewage is sprayed over the trickling filter, a large bed of coarse, impervious material; as it trickles down through the bed, it comes into contact with the ambient air, which promotes bacterial action;[29] from there it passes to the final clarifier. Odors and other organic materials are emitted from the clarifiers and the filter.

Sludge collected in the clarifiers is frequently digested to render it more innocuous. In the BRD, a process has been developed for sludge composting. Two plants are under construction for cities with populations from 50 000 to 80 000. Digestion generates a gas with approximately 75 percent methane, 20 percent carbon dioxide, and a balance of oxygen, nitrogen, and trace contaminants. Since the gas has a heating value of about 25 MJ/m^3, it is frequently burned in a boiler or in an internal combustion engine at the plant.[29] Either direct venting or improper combustion of this gas will result in organic emissions.

Table 3-6. - ORGANIC VAPOR CONCENTRATIONS EMITTED FROM AN ACTIVATED SLUDGE PLANT

Process	Concentration, $\mu kg/m^3$
Bar screen	35.2
Aeration tank	20
Final clarifier	6.7

Hydrocarbon emissions vary widely from plant to plant depending on the type of plant and treatment process, the size of the plant, and the conditions and composition of the influent. The activated-sludge treatment plant is probably the largest emitter of hydrocarbons among the three plant types. However, quantitative data on the amount of emissions are difficult to obtain because treatments are essentially outdoor operations.

3.2.12 Waste Incineration and Other Burning

Preliminary results of a survey conducted by the U.S. Public Health Service indicate that household, commercial, and industrial solid waste production per capita in the United States is about 4.5 kg/day; this totals to 330 Gkg/yr. About 170 Gkg/yr (or 2.5 kg/day per capita) is collected for disposal, and the remainder is either disposed of on site or handled by the household or establishment itself;[30] an estimated 160 Gkg is burned in the open or in incinerators.[1] An additional 250 Gkg of agricultural waste and 1 Tkg of mineral wastes are generated each year;[30] half of the agricultural waste is burned in the open, and 245 Gkg of coal refuse are consumed by fire each year.[1] The quantity of material consumed by forest burning and structural fires is about 90 Gkg and 146 Gkg a year, respectively.[1]

Incineration and open burning, used to reduce the weight and volume of solid waste, can cause organic emissions from incomplete combustion. Open burning of refuse is the greatest offender, but inefficient incinerators are also significant sources. Hydrocarbon emissions from both sources are estimated as shown in Table 3-7. About 0.18 Gkg are emitted annually from uncontrolled forest fires[1] caused by lightning or by

Table 3-7. - ESTIMATED EMISSIONS FROM INCINERATION AND OTHER BURNING IN THE UNITED STATES, 1968[31]

Emission source	Quantity, Mkg/yr	Hydrocarbon emissions, Mkg/yr
Onsite incineration	52 000	26.4
Municipal incineration	14 500	1.8
Conical burner incineration	24 500	136
Open burning	70 000	1 040
Agricultural burning	250 000	1 500
Controlled forest burning	70 000	690
Forest wildfires	132 000	1 320
Structural fires	7 300	72.5
Coal refuse fires	43 500	218
Total	663 800	5 500

Table 3-8. - WASTE IN THE BRD, 1970[32]
[Gkg]

Source	Quantity
Household	16[a]
Commercial	4
Industrial	2
Building refuse	5
Mining and steel industry	20
Settle tank mud	18
Automobile wrecks	1
Agricultural waste	190
Total	260

[a] About 20% incinerated.

careless practices. Forest debris, crop residue, scrub, brush, weeds, grass, and other vegetation, burned for one or more of the following purposes--to control vegetation, insects, or organisms harmful to plant life; to reduce the volume of waste; to minimize fire hazards; or to improve land--emit about 0.27 Gkg/yr.[1] An estimated 62 Mkg of hydrocarbons are emitted each year from 0.54 km^3 of burning coal refuse.[1] Structural fires emit an estimated 61 Mkg of hydrocarbons annually.[1]

In the BRD household, commercial, and industrial waste production totals 22 Gkg per year. Data for these and other sources are shown in Table 3-8. Figures 3-4 and 3-5 show the trend in the BRD in waste handling and disposition.

3.2.13 Miscellaneous Industrial Sources

Almost any processing of organic matter results in the emission of hydrocarbons. Chocolate manufacturing, bread baking, pharmaceutical manufacturing, leather tanning, coffee roasting, food processing, fermentation, tobacco aging, and charcoal manufacture all emit hydrocarbons; quantitative information is not generally available.

The manufacture of fermented beverages, such as beer, wine, and whiskey, largely results in the emission of alcohols from distilling operations, cooking or brewing kettles, vacuum systems, fermenters, and aging or storage processes.

Drugs and pharmaceuticals range from purified anesthetic-grade ethers and other anesthetics to extracted, purified cod liver oil. Pill coating with chocolate or other taste-controlling materials, can emit odors that are annoying if they persist.

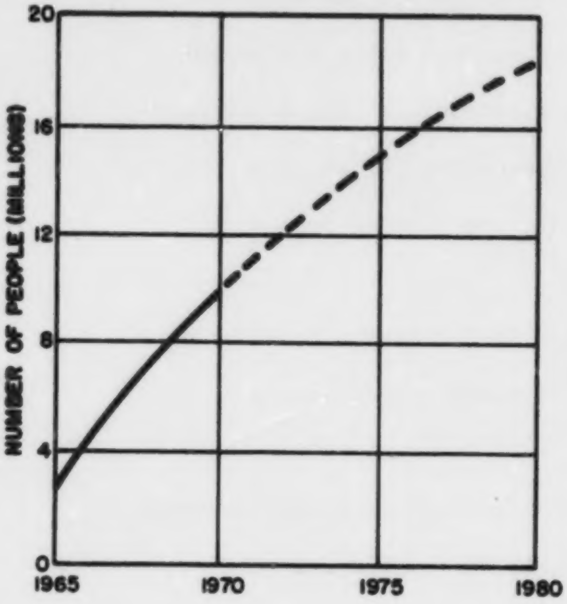

Fig. 3-4. Number of inhabitants served by community waste incinerators in the BRD.[32]

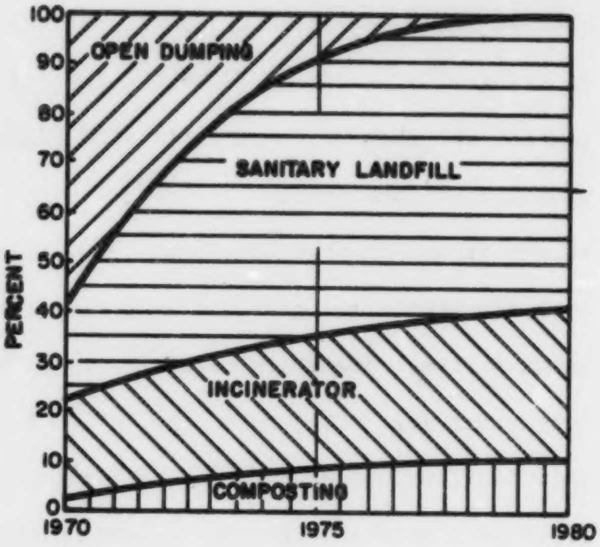

Fig. 3-5. Projected development of method of disposition of household waste.[32]

Food processing, such as deep fat frying (french frying) of baked goods, vegetables, fish, and meat, results in the vaporization of oils from the food; excessive heating of the cooking oil vaporizes some of the oil itself.[10] Coffee roasting releases odorous organic compounds from the volatile matter in green coffee beans.

The canning of fish and other perishable foods results in hydrocarbon emissions from the oils and fats; the canning of fish is probably most objectionable because of the odorous compounds emitted. Fish may be either cooked before canning (large fish like tuna) or canned, cooked, sealed, and then pressure cooked (sardines, anchovies, etc.). Condensed steam, oils, and juices from the cooking are collected for byproduct recovery; and the inedible parts of fish are processed into byproducts such as fish meal, high-protein concentrates, and fish solubles. Reduction of the inedibles produces the major organic odorous emission, trimethylamine, $(CH_3)_3N$.

Charcoal, wood alcohol, and acetic acid are produced by the destructive distillation of wood--by heating hard wood in an enclosed retort. Approximately 20 kg of methane and other noncondensible organic compounds are emitted for each cord of wood (1 800 kg).[13] Since this gas contains about 27 percent carbon monoxide and has a heating value of 5 600 to 9 300 kJ/m^3, it is usually burned as fuel at the plant.

In waste composting, emission of hydrocarbons can be reduced by filtering the gases through beds of earth by means of which the gases are biologically oxidized.

The malodorous gaseous emissions from rendering plants can be controlled by scrubbing with limestone slurry with chlorine addition or by treating the scrubber effluent in a separate plant.

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4. CONTROL TECHNIQUES (HARDWARE)

4.1 INTRODUCTION

Methods now employed commercially to control the emission of organic air pollutants are (1) changes in operations or processes, (2) substitution of a higher-boiling-point material and/or a less reactive compound in the process, and (3) installation of control devices (incinerators, adsorbers, absorbers, and condensers). For condensable hydrocarbons, particulate control techniques are applicable. By far the most important control technique is to design basic equipment for utilizing efficiently or consuming completely the materials being processed. For stationary combustion sources this is the most cost-effective technique. Failing this, control devices must be used to reduce organic emissions.

Basic operating principles of control devices are explained, areas of application are indicated, and significant factors affecting operation are outlined.

4.2 INCINERATION

Incineration is a widely used technique for controlling organic emissions by combustion. The objective is to oxidize vapors and gases to harmless products such as carbon dioxide and water. Some emissions contain combustible particulates that can also be oxidized. Others contain substances that oxidize to harmful pollutants. Where it is applicable, incineration offers the potential of heat recovery.

Devices in which dilute concentrations of organic vapors are burned by adding fuel are known as afterburners. Devices used to burn waste gases that have sufficient heating values to burn without added fuel are known as flares if there is no air premixing, or as incinerators if there is air premixing.

4.2.1 Afterburners

The two types of afterburners are direct flame and catalytic. Under the right conditions, the firebox of a process heater or boiler may be used as an afterburner.

4.2.1.1 Direct-Flame Afterburners—Direct-flame afterburners use a flame to complete the oxidation of organic emissions. Flame coverage, turbulence, residence time, and temperature are important in their design. Removal efficiencies can be as high as 95 percent; secondary disposal problems are not usually encountered. Operational costs are high unless heat recovery equipment is installed.

To achieve complete combustion, thorough mixing of the organic vapors and oxygen is required; high turbulence or injecting steam promotes this intimate contact. If the combustion reaction rate is slowed by insufficient temperature, insufficient burning time, or poor mixing, carbon monoxide, aldehydes, and other products of incomplete combustion may be produced.

Generally, for safety, high concentrations of combustibles are diluted to 25 percent or less of the lower flammability limit, and the required heat is provided by adding a second fuel. The technique is to inject enough fuel gas into the air-rich effluent to bring a portion into the combustible range and to heat the remainder to the ignition temperature. Thus, added energy starts a chain reaction wherein heat from the burning vapors supplies a portion of the total heat required to complete the chemical reaction.

Equipment description--Both the burner use and the overall combustor design must be considered to achieve optimum mix, temperature, and time for combustion. Figure 4-1 shows a multijet burner arrangement wherein the effluent gases are used as both primary and secondary air. Figure 4-2 shows a complete afterburner with this type of burner. Figure 4-3 illustrates a multijet burner arrangement in which no air is mixed with the gas before injection into the combustion zone; distribution of multiple small raw-gas jets over the duct area results in efficient mixing of the effluent with the flame. Figure 4-4 shows an afterburner with heat exchanger, in which the afterburner exit gases preheat the gas stream containing the pollutants that are to be burned.

Operational factors--The mixture of air and combustibles must provide enough heat to reach and maintain the combustion temperature. The accumulated thermal energy in the mixture at the lower flammable limit is, gnerally, equivalent to approximately 1.9 MJ per normal cubic meter. At ambient temperature, then, the organic vapors and liquids in the air must provide at least 1.9 MJ/Nm^3 for a flame to be initiated by a high-temperature source and to be self-sustaining.

The oxidation rate is a function of temperature. Oxidation can be carried out either above or below the autoignition temperature of a vapor. However, an outside source of heat energy must be provided to maintain the temperature and the reaction rate, unless (1) the vapor concentration is high enough to support self-sustained combustion and (2) an ignition source is maintained. Limiting values for different mixtures are determined by the heat of reaction, the thermal conductivities, rates of diffusion, and specific heats of the components.

Burning time, called "dwell time", "residence time", and "retention time", varies with the type of effluent and the technique of incineration from 0.3 to 0.6 second at 920 to 1 033 K. Burner type and arrangement also effect burning time. The better the flame contact (or coverage) with the effluent gases, the shorter the time required for complete combustion. Turbulence in the combustor zone also reduces required retention time. Multijet burners have effective flame contact.

Properly designed and operated direct-flame afterburners usually achieve organic vapor removal efficiencies in excess of 95 percent. The materials of construction must be structurally adequate in terms of thickness, weight, etc., or thermal stress will lead to equipment failure.

In practice, it is usually unwise to control, solely by combustion, organic vapors that contain halogens or sulfur, since the products are usually less desirable and often corrosive; therefore, a secondary control system such as a series of scrubbers may be required to remove contaminants from incineration.

Typical applications—Afterburner control devices have been applied successfully to aluminum chip dryers, petroleum processors, animal blood dryers, automotive brakeshoe debonding ovens, citrus pulp dryers, coffee roasters, wire enameling ovens, incinerators, foundry core ovens, meat smokehouses, paint-baking ovens, and varnish cookers. Other applications include paper printing and impregnating, pharmaceutical manufacturing, sewage disposal, chemical processing, and textile finishing. In many of these operations, the afterburners reduce the amount of particulate matter as well as the organic vapors present in the gas stream, and thereby reduce the opacity of the gas.

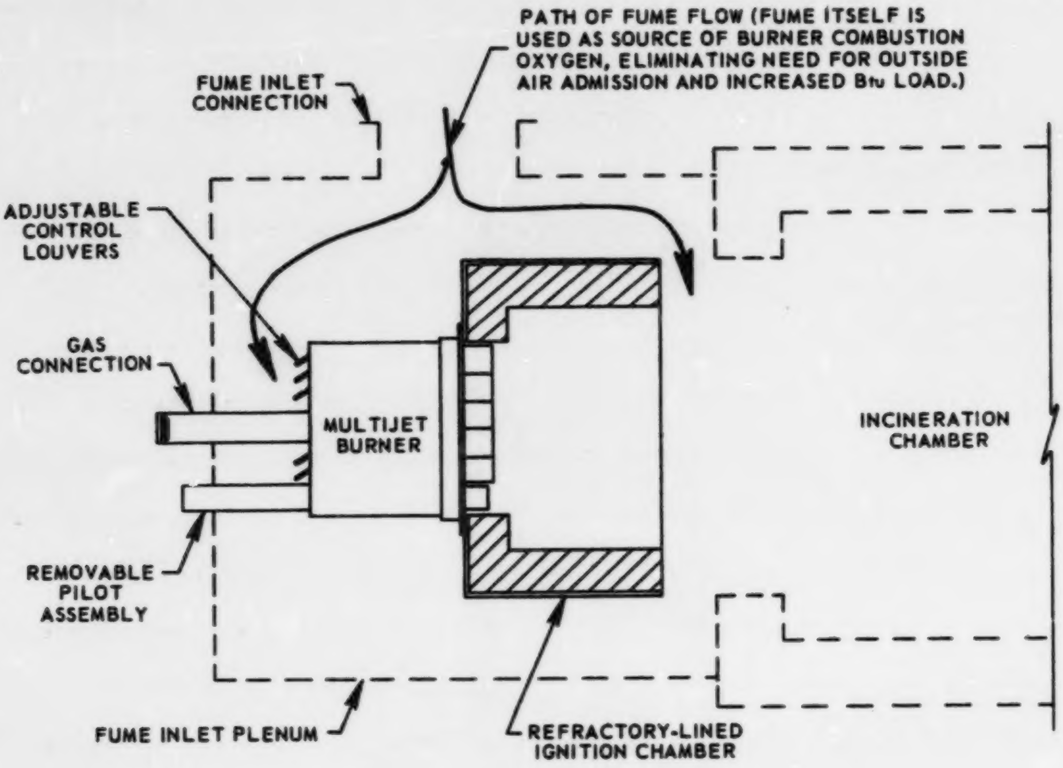

PATH OF FUME FLOW (FUME ITSELF IS USED AS SOURCE OF BURNER COMBUSTION OXYGEN, ELIMINATING NEED FOR OUTSIDE AIR ADMISSION AND INCREASED Btu LOAD.)
FUME INLET CONNECTION
ADJUSTABLE CONTROL LOUVERS
GAS CONNECTION
MULTIJET BURNER
INCINERATION CHAMBER
REMOVABLE PILOT ASSEMBLY
FUME INLET PLENUM
REFRACTORY-LINED IGNITION CHAMBER

Fig. 4-1. Typical multijet burner arrangement used in direct-flame afterburners.

4.2.1.2 Catalytic Afterburners—Catalytic afterburners, designed much like direct-flame types, employ a solid active surface whereon the combustion reaction takes place. Since they can be operated at temperatures much lower than those required for direct-flame combustion, catalytic afterburners have the advantage of lower fuel costs in some applications; however, since fuel requirements for a direct-flame afterburner can be lowered by using a heat exchanger, the total costs may be comparable. Two catalytic afterburners used in the BRD are shown in Figs. 4-5 and 4-6.

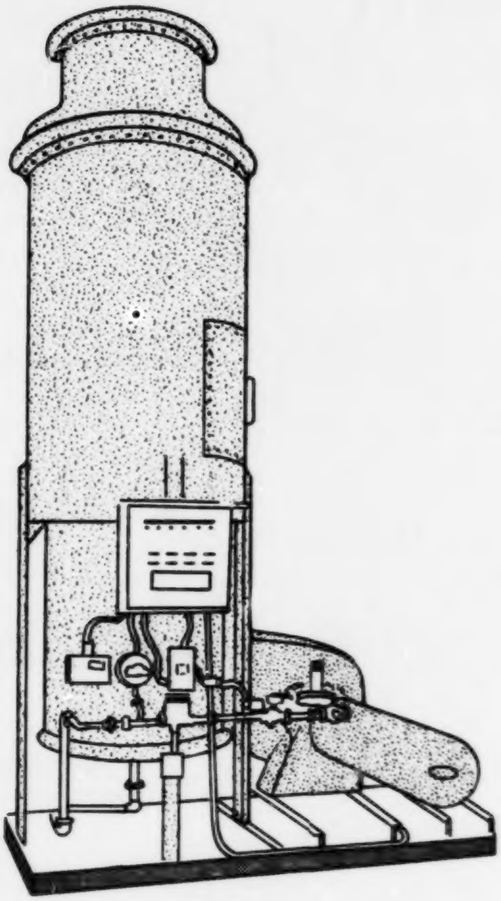


Fig. 4-2. Direct-flame afterburner, vertical arrangement .

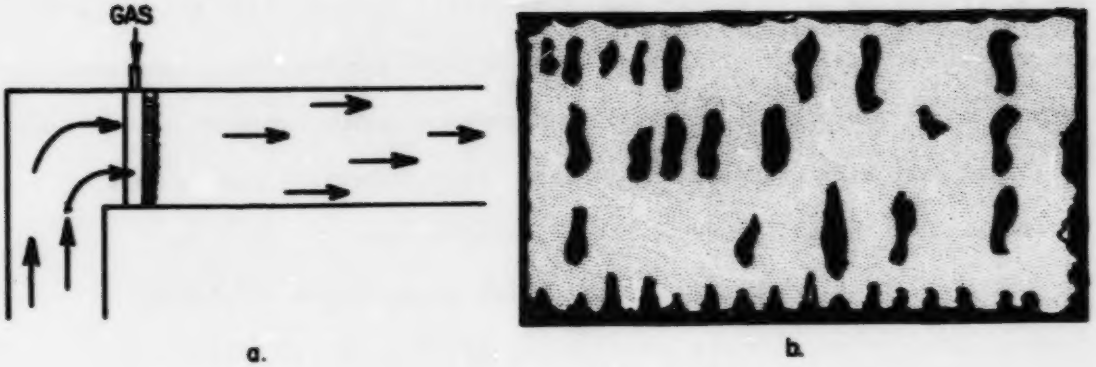


Fig. 4-3. Raw gas burner and multiple-jet grid.

a. Diagram showing location of burner.
b. Drawing of burner during operation.

Catalytic incineration can be applied to very low concentrations of contaminants, limited only by the prescribed temperature limits of the catalyst and related equipment.

The primary disadvantages of catalytic afterburners are high maintenance costs, the fact that they cannot be readily used for mixtures, and susceptibility to catalyst poisons. They will not function if the catalyst has become fouled or deactivated by particulate matter, by polymer coating during low-temperature operation or by surface erosion caused by heat effects. If catalyst poisons are present in the waste gas stream, flame afterburners should be used. Catalyst life is generally two years. An afterburner that does not achieve substantially complete combustion of the organic emissions can produce carbon monoxide, aldehydes, and other partially oxidized substances. These materials may be less desirable than the emissions without an afterburner.

Catalytic incineration has application in petroleum refining, chemical processing, foundry core baking, fabric coating, baking ovens and others.

4.2.1.3 Process Heaters and Boilers--Fireboxes of heaters and boilers can approximate the conditions of well-designed afterburners, if the temperature, turbulence, and flame contact are adequate. If the gas stream to be treated contains appreciable heat, special fireboxes (waste heat boilers) are used. If the heat content is low, common types of steam and hot water heaters and boilers are used.

Completely satisfactory adaptations of boilers for use as afterburners are not common. The primary function of a boiler is to supply steam or hot water; whenever its use as a control device conflicts with this function, one or both of its purposes suffer. All aspects of operation should be

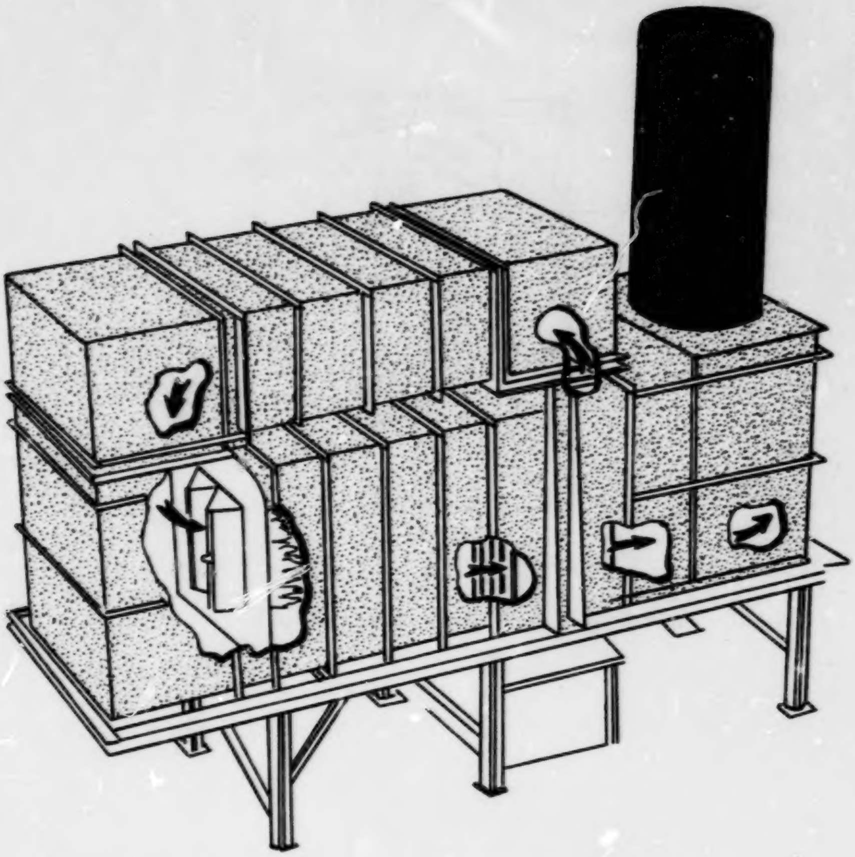


Fig. 4-4. Afterburner with heat exchanger .

thoroughly evaluated. Use of a boiler as an afterburner requires that the following conditions exist:[1]

1. Air contaminants must be almost wholly combustible; noncombustible pollutants (inorganic dusts and fumes) deposit on heat transfer surfaces, foul them, and cause losses in boiler efficiency and steam-generating capacity.
2. Volumes of contaminated gases must not be excessive; excesses reduce thermal efficiences, cause high pressure drops through the system, and in some cases, exceed the draft provided by boiler auxiliaries.
3. Oxygen content of the contaminated gases must be similiar to that of air to prevent incomplete combustion and resulting formation of tars

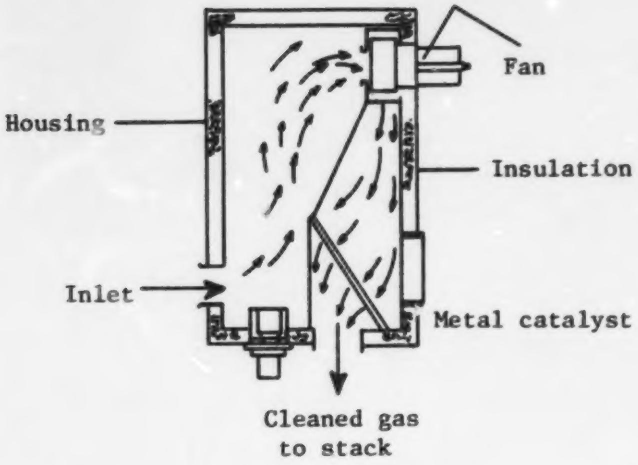
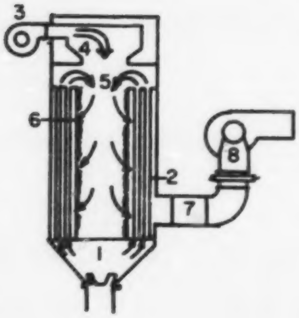

Fan
Housing
Insulation
Inlet
Metal catalyst
Cleaned gas
to stack

Fig. 4-5. UPO-Kavag system.



1	Inlet
2	Heat exchanger
3	Add. heater
4	Burning chamber
5	Mixing chamber
6	Catalyst
7	Cleaned gas to stack
8	Fan

Fig. 4-6. Decatox system .

or resins which will deposit on heat-transfer surfaces and reduce boiler efficiency; if the contaminant concentrations exceed air pollution control standards for gas- or oil-fired boilers, tube fouling will become a major maintenance problem.

4. Adequate flame must be maintained continuously: high-low or modulating burner controls are satisfactory if the minimum firing rate is sufficient to incinerate the maximum volume of effluent expected in the boiler firebox, but obviously on-off controls are not.

These requirements can be considered in the design of a new boiler to be used as an afterburner.

4.2.1.4 Selection of an Afterburner--If an afterburner is being considered as a means of controlling organic contaminants, the following information must be determined.

1. The chemical contaminant must be identified or tested to make sure it will burn completely, without yielding objectionable products of combustion; when objectionable products are formed, the control system must employ equipment in addition to afterburners.
2. The concentration and physical form of the contaminant must be determined to help estimate the amount of heat to be supplied; liquid mists or solid materials may preclude the use of catalytic afterburners and fireboxes of heaters and boilers.
3. The temperature of the effluent to be controlled must be determined to help estimate the needed auxiliary heat and fuel and the final volume of gases in the afterburners.
4. The volume rate of the effluent must be known to set the rate of auxiliary fuel and to determine the dimensions of the afterburner: throat velocities of 4.5 to 7.6 m/s can provide adequate mixing of contaminated gases with flames of burner combustions products; for a

single-nozzle burner, velocities of 12.1 m/s can enhance turbulence and mixing; combustion chamber velocities are usually 3.1 to 4.5 m/s to allow sufficient retention time and sufficient turbulence for complete combustions while maintaining a reasonable length for the afterburner.

5. The oxygen content of the effluent must be known to determine whether there will be sufficient quantity for complete combustion of the contaminants and any extra fuel.
6. The space limitations must be considered in designing the afterburner.
7. Weight limitations must be considered because afterburners may require additional structural support.
8. The cost of electric power and gaseous fuels must be considered because they contribute significantly to the total operating costs of the equipment.

To select a catalytic afterburner, a good general rule is to consult with a catalyst manufacturer on the most suitable catalytic equipment configuration. Among the many basic catalytic materials are ceramic, metallic pellets, and honeycombs. Metallic and metallic compound coatings include platinum, platinum alloys, copper chromite, copper oxides, chromium, manganese, nickel, and cobalt.

4.2.2 Flares

Smokeless flares are of two types--elevated flares and ground-level. Elevation safely dissipates the heat released and diffuses any vapors that may be emitted. In an elevated flare, smokeless combustion is achieved by the injection of an inert gas to the combustion zone to provide turbulence and to inspirate air. It is noted, however, that the smokeless combustion achieved will be accompanied by an increase in unburned hydrocarbon emissions. The most commonly used air-inspirating material is steam.

Smokeless combustion can be expected only if there is (1) sufficient fuel value in the gas mixture to obtain the minimum theoretical combustion temperature, (2) adequate combustion air, and (3) adequate mixing of the fuel and air.

Steam injection is believed to have several advantages: (1) energy is at relatively low cost to inspirate air and provide turbulence within the flame; (2) steam-fuel reactions form oxygenated compounds that burn readily at relatively low temperatures; (3) waste-gas reactions have this same result;and (4) steam reduces the partial pressure of the fuel and retards polymerization. A disadvantage of steam injection is an increase in unburned hydrocarbon due to reduced flame temperature.

4.2.2.1 Elevated Flares--Three types of steam-injected elevated flares are in use. The differences among them are the manner in which the steam is injected into the combustion zone.

Equipment description--In the first type, steam is injected by several small jets placed concentrically around the flare tip and installed at an angle to discharge the steam in a converging pattern immediately above the flare tip. A second type has a flare tip with no obstruction to flow; that is, the flare tip is the same diameter as the stack. The steam is premixed with the gas before ignition, being injected by a single nozzle located concentrically within the burner tip. In a third type, a flare tip causes the gases to flow through several tangential openings to promote turbulence, and a steam ring at the top of the stack has many equally spaced holes about 3 mm in diameter for injecting steam into the gas stream.

Operational factors--The injection of steam can be controlled either manually or automatically. In some installations, the steam is injected at maximum rates, and manual throttling of a valve is required to adjust the steam flow to the gas flow. A pressure-sensing control element in the gas line actuates a control valve in the steam supply line; a small bypass valve is usually used to permit a small, continuous flow of steam to keep the steam holes open and permit smokeless burning of small gas flows. A mechanical air-mixing system would be ideal, but not economical because of the large volume of gases handled.

4.2.2.2 Ground-Level Flares--Ground-level flares are of four types: horizontal venturi, water injection, multijet, and vertical venturi. In a horizontal venturi system with its groups of standard venturi burners, the gas pressure inspirates combustion air for smokeless operation. A water injection flare has a single burner with a water spray ring around the burner nozzle; the spray inspirates air and provides water vapor for smokeless combustion. For controlling smoke, water is not as effective as steam for high gas flow rates, unsaturated materials, or wet gases. A multijet flare uses two sets of burners--one for normal gas release rates and both for high rates. A vertical venturi flare, like a horizontal flare, uses venturi burners; this type is suitable for relatively small gas flows at a constant rate.

4.2.3 Recent Developments in Incineration

Thermal and catalytic oxidation are the predominant methods of incineration used to control air pollution. A third method, direct flame incineration, may be considered when the exhaust contains such high heating value that it may be considered a fuel. However, the majority of exhausts involve low concentrations of odorous hydrocarbons that are unsuitable for use as fuels.

4.2.3.1 Thermal Incineration--Thermal incineration has been recommended almost unanimously within the literature for controlling emissions from varnish kettles, due to the complex chemical composition of the fume stream.[2-7] Where the system employed uses an afterburner, the burner is often preceded by a wet scrubber. Earlier investigators have stressed the importance of a luminous flame in the afterburner for greater heat transfer.[2,8] Their recommendations appear to have been based upon work by Hottel.[9] This work deals with the increased overall heat transfer coefficient due to radiation between a luminous flame and a black body or a gray body with a high absorptivity. It would apply more correctly to a furnace or to a fume stream composed primarily of particulates than to organic vapors. Other investigators have stated that heat transfer is best achieved by mixing (turbulence) when vapors are burned, and best achieved by radiant heat transfer when particulates are burned.[10] The very nature of luminous flame burners precludes turbulent mixing.

The performance of afterburners specially designed to employ turbulent mixing has recently been reported by DiGiacomo.[11] Two approaches were used: an integral-blower burner and a non-powered raw gas burner. The integral-blower burner was a nozzle-mixing type with a cast iron mixing cone to stabilize the flame so that the fume stream could be introduced at high velocity. The non-powered burner was mounted directly in the fume stream, with baffles to force the stream through mixing plate openings. Both systems were tested using a fume stream from a wire enameling operation, with odor being the main air pollution

Table 4-1. - COMPARISON OF NEW AND CONVENTIONAL AFTERBURNERS

Parameter	Integral-Blower Burner	Non-Powered Raw Gas Burner	Conventional Approach
Exhaust volume, Nm^3/s	0.24	0.10	0.45
Maximum heat input, kJ/s	234	103	580
Fuel consumption, Fuel/exhaust	0.026	0.026	0.032
Residence time, sec.	0.67	0.50	0.7
Mixing velocity, m/s	18.3	17.1	8.8
Operating temperature, K	950	950	930
Length-diameter ratio	1.6	1.25	4

problem. Odor was completely eliminated when firing with a stoichiometric fuel-air ratio. Under luminous-flame conditions, some odor was eliminated, while excess-air firing produced aldehydes, thus compounding the odor problem.

Three commercial systems, based upon the integral-blower concept have been operated in a New Jersey plant for two years. Four non-powered raw gas systems are currently in operation in Ohio.[11] Table 4-1 compares the performance of these systems with the conventional system described by Mills et al.[8]

The new approach achieves almost a 100-percent increase in mixing velocity; reduces fuel consumption 20 percent; reduces residence time by 29 percent (non-powered burner only); and significantly reduces length-diameter ratio.

4.2.3.2 Catalytic Incineration--Catalytic combustion offers the potential of pollution control at low temperatures, saving fuel.[12] The reduction in temperature that catalysts make possible is often substantial. Some examples, given by Edwards[13] are:

Emission	Catalytic Oxidation	Auto Ignition
Carbon monoxide	470 K	920 K
Solvents	640 K	920 K
Hydrogen	360 K	920 K
Methane	780 K	920 K

While a broad range of catalysts are currently being evaluated, in nearly every instance the most effective catalytic agents for air pollution control are precious metals--either platinum or palladium.[14-16] Acres has determined the ignition temperatures (minimum temperatures for any significant reaction to occur) on ceramic-honeycomb-supported platinum catalysts (Matthey Biship THT catalyst) for a wide range of molecules often encountered in polluted air.[17] Table 4-2 shows these temperatures and the inlet temperatures required for 90-percent conversion of the pollutant by the catalyst.

The temperature required for high conversion of fumes depends of course on the ignition temperature, the space velocity, and the type of catalyst. The concentration of organic compounds is also important. In most cases, the concentration does not significantly affect the ignition temperature. A notable exception, however, is methane. The concentration and its composition does, however, determine the amount of oxygen that will be consumed and the temperature rise that will occur. For example, when natural gas components are burned, the temperature rise (ΔT) across the catalyst bed is 383 to 394 K for every 1 percent oxygen consumed.

Precious metal catalysts are prepared for use by one of the following methods: deposited on a ceramic support that has a pelleted configuration: deposited on a ceramic support that has a honeycomb configuration; electro-deposited on a metal support and fabricated in a mat form.[16,18,19] Manufacturers have concentrated on the development of the latter two kinds. No applications of fluidized solid precious metal catalysts have been reported.

While precious metal catalysts are prodominant, other catalysts are being evaluated. Bauxite and iron ore have been reported to be effective at 673-873 K for removal of asphaltines, paraffins, naphthenes and aromatic compounds contained in waste gases from the production of high-temperature pitch.[20] A copper-chromium catalyst, tested experimentally, has removed organic substances from waste from varnish production.[21] The gases contained acrolein, phthalic anhydride, and xylene. Malinksy used a microreactor to determine the activity of metal oxides, precipitated onto gamma aluminum oxide carriers, in the catalytic combustion of methane.[22] Oxides of

Table 4-2.-IGNITION TEMPERATURES ON THE CATALYST FOR MOLECULES ENCOUNTERED IN POLLUTED AIR

Molecule	Ignition Temperature, K	Inlet Temp. for 90% Conversion, K
Hydrogen	293	293
Carbon monoxide	423	423-473
Benzene	453	523-573
Toluene	443	523-573
Xylene	473	523-573
Alpha pinene	463	523-573
Mesityl oxide	453	523-573
Ethanol	433	523-573
n heptane	433	523-573
Methyl isobutyl ketone	448	573-623
Methyl ethyl ketone	448	573-623
Dimethylformamide	473	623-673
Ethyl acetate	548	673-723
Methane (air)	573	723-773
Methane (3% O_2/N_2)	673	723-723
Thiophen	608	673-723
Pyridine	680	673-723
Chlorobutane	698	723-773
Hydrogen sulphide	673	673-698
Carbon disulphide	623	648-673

cobalt, chromium, copper, manganese, and iron were studied. Of these chromium and cobalt were the most stable. Complete combustion was not obtained. Alanova conducted laboratory tests of alloy catalysts containing nickel, chromium, manganese, copper, iron, cobalt, and silicon in various combinations and ratios to determine their effectiveness in removing acetone, ethanol, benzene, toluene, and xylene from a vapor-air mixture.[23] His chromium-nickel alloys were most effective, giving complete oxidation of ethanol and xylene at 623–723 K with a volumetric gas flow rate of 20 000 to 70 000 reactor volumes per hour.

There are certain contaminants that under certain conditions or in sufficient concentration have been shown to affect the life of catalysts. These fall into three categories: catalyst poisons such as phosphates, arsenic compounds, and heavy metals; reaction inhibition such as the halogens and sulfur compounds; fouling agents or masks such as ceramic dusts, iron oxides, carbon, oils and silicons. Contaminants may pose serious problems that can often be overcome by an efficiently designed system and an effective catalyst maintance program.

4.2.[illegible] Flame Afterburners--A British study has been conducted to improve the design of commercial direct flame type incinerators.[24] A sur[illegible] incinerator was designed as a very rugged, heavy duty type of combustion system for high temperature operation. It is equipped with a pair of burners firing tangentially at the combustion end to form a circular "hot track" of burner gases in a restricted area. An injection nozzle is located axially at this point to introduce the process effluent under pressure directly into the burner combustion track.

The purpose of the jet incinerator is not only to incinerate the hydrocarbons, but also to develop a suction to entrain the fumes without requiring external exhausters or fans.

4.2.3.4 Oil and Gas Furnaces--The problems of emissions control for oil and gas furnaces have been approached in two ways: fuel additives and equipment design. A propane diffusion flame was used by Cotton to examine the mechanism of soot removal by metallic additives.[25] Efficiencies of soot removal were determined for 40 metals, and a semiquantitative mechanism was proposed for the alkaline earth metals, barium, strontium, and calcium. These metals undergo a homogeneous gas phase reaction with flame gases to produce hydroxyl radicals which rapidly remove soot or its precursors. The proposed mechanism is supported by measurements of free-radical recombination catalysis by the alkaline earths in premixed hydrogen-oxygen-nitrogen flames.

Martin investigated the use of additives with domestic oil furnaces.[26] He tested ferrocene (dicyclopentadienyl iron), ethyl 2 (methylcyclopentadienyl manganese tricarbonyl), and fuelco SO_3 (84 percent C, 13.1 percent, 1.5 percent Mn),using three high-pressure atomizing distillate oil burners. Each additive reduced carbon (smoke) emissions. They did not reduce emissions of carbon monoxide, unburned by hydrocarbons, or nitrogen oxides. They produced emissions of metallic particulates. Moreover, results indicated that the more efficient the burner, the less the reduction in smoke.

A standard screening procedure has been established for testing additives in a distillate-oil-fired test furnace.[27] Using this procedure, most of the known additives were evaluated. Results showed that a majority of the proprietary additives tested had no beneficial effects on air pollutant emissions from the test system. Some additives increased particulate emissions. Some that contained metals gave indications of reducing particulate emissions. None of the additives reduced sulfur oxides, and only three appeared to reduce nitrogen oxides even marginally. Nitrogen in an additive significantly increased emissions of nitrogen oxides. The authors conclude that there is need for careful study of other factors such as fuel and furnace effects, optimum dose, cost-effectiveness, and toxicology of the resultant metallic particulate emissions. Meanwhile, additives have not been shown to offer clear cut advantages for emissions control.

The Bureau of Mines had studied the concentrations of residual hydrocarbons, the decay of carbon monoxide, and the formation of nitrogen oxides in the secondary combustion zones of propane-air and methane-air flames; three enclosed burners were used to simulate gas appliances such as space and water heaters.[28] Based on this study, four principles were derived that, applied to gas appliance design, would help insure minimal emissions of these air pollutants: 1) oxides of nitrogen can best be kept low by depressing peak temperatures to about 1950 K; 2) if this is not possible, then the secondary combustion zone should be cooled rapidly to this temperature; 3) carbon monoxide concentrations can be limited by rapid induction of secondary air; 4) hydrocarbon concentrations can be controlled by designing for well-seated, stable flames. For oil-fired furnaces, Hagel has reported the development of a compact unit to enhance the competitiveness of oil heating and to accommodate future pollution control requirements.[29] The furnace has a fuel atomizer which creates a uniform fog of fuel for combustion. Other key components are improved warm air heat transfer in the combustion chamber, a heat exchanger capable of reducing stack temperatures to 450 K, a radial blade fan insuring stable combustion air, and an integrated replaceable burner. The efficiency of a prototype furnace was 86 percent at a nominal 105 MJ/hr output. This represents a gain of 10-15 percent over conventional furnace operations. Emissions of hydrocarbons, carbon monoxide, and nitrogen oxides were eithin future anticipated limits. The furnace appears to have cost advantages also.

Howekamp and Hooper investigated effects of combustion-improving devices for high-pressure atomizing-gun burners used in domestic oil-fired furnaces.[30] Five commercial devices were installed in a typical warm-air furnace and tested for their effects on emissions of smoke, carbon monoxide, total gaseous hydrocarbons, and nitrogen oxides. Three of these improved the performance of a new, well-designed burner, as indicated by lower smoke levels and higher operating efficiencies. The best of the three effective devices incorporated an air shield to control excess air and to cause the flame to be retained at the end of the blast tube.

4.2.3.5 Solid Waste Incineration--A study of apartment house incinerators has identified certain operational deficiencies.[31] Burning at rated capacity could not be achieved in several units because of high grate loadings. In all units tested, combustion temperatures were below the 920-1033 K range required for destruction of volatile and odorous material. The single-chamber units had unacceptable particulate emissions compared to representative emission regulations. The multiple chamber units had considerably lower particulate emissions, and the best performance was achieved by those units that operate with primary chamber draft between 24.9 and 62.2 N/m^2. It is recommended that apartment-house incinerators be designed with multiple chambers, double flues, forced overfire air and draft control, gas washers, charging gates, primary and secondary auxiliary burners, and a programming system.

The incineration of industrial wastes containing plastic wastes and rubber has been the subject of some special studies. Yamada evaluated a heat-bath carbonization system for mixed plastic wastes that generate hydrogen chloride.[32] The system takes advantage of the fact that polyvinyl chloride breaks down at comparatively low temperatures. Melted plastic wastes provide the heat for carbonization. The resulting gases are then subjected to byproduct recovery and incineration. Ichikawa has evaluated a pretreatment method for polyvinyl chloride wastes which involves dry distillation in an oxygen-free kiln at a stable temperature of 550 K.[33] Most of the hydrogen chloride is discharged and recovered as chlorine. The residue is burned. Sakamoto describes a four-stage fluid bed incinerator used for the disposal of old tires and synthetic rubber scraps.[34] Inside the first incinerator chamber a stirring arm rotates slowly. The combustion air is blown out through many holes in this arm. The burner in the first chamber is used only for ignition, while the old tire and rubber scraps are completely burned in the second chamber. Air is blown into the second chamber from above and below. Waste or other solvents can be burned together with solvent inflammables in the second chamber. The third and fourth chambers keep the gases until they burn completely. High temperature gas issuing from the fourth chamber is cooled with sprayed water and emitted from the stack by a blower. The third and fourth chambers were shown to be effective in controlling emissions of black smoke and ash.

4.3 ADSORPTION

Adsorption is the collection of organic vapors upon the capillary surfaces of a solid adsorbent, which is usually activated carbon. After the carbon bed has adsorbed the optimum amount, the gas stream is diverted and the bed is steam stripped to remove the collected material; then, steam and the material are condensed, and the organic material is recovered by decantation or distillation. Because of the need to recover the adsorbent, two or more carbon-containing vessels are employed, one to adsorb while the other is being steam cleaned.

Installation and operating costs of adsorption systems are high, but recovery of valuable materials may compensate for the extra cost. High removal efficiencies are possible, but resin-forming gases cannot be handled because they plug the carbon beds.

The two main types of adsorption are physical adsorption, in which the gas is attracted to the surface of the adsorbent, and chemical adsorption, in which the gas interacts with the adsorbent. Surface attraction is due to van der Waals' forces, the intermolecular forces that condense a gas to the liquid state. On a smooth surface, the adsorbed layer is not more than a few molecules thick; within the capillaries of a porous solid, this surface adsorption is supplemented by capillary condensation, so the total amount adsorbed is substantially greater.

In vapor-phase adsorption, the exothermic gas-solid equilibrium is governed by the rate of adsorption. Conditions that shift the equilibrium toward saturation usually improve the process. Consequently, the system is more efficient near the dewpoint of the adsorbate (substance being absorbed) and when it is at the highest pressure and the lowest temperature within the process limitations.[35]

Certain granular solid attract and retain selected components of a fluid on their surfaces. The amount adsorbed is usually small; however, certain materials (e.g., activated alumina, silica gel, and activated carbon) adsorb substantial quantities of gases and vapors. These materials are highly porous and thus have a large surface-to-volume ratio, which allows a fluid to penetrate the large surface area; their preferential affinity for specific substances determines their industrial applications.

All adsorbents are capable of adsorbing organic solvents, impurities, and water from gas streams, but each has a particular affinity for either polar or nonpolar vapors.[36] Water vapor is a polar compound. Organic vapors are nonpolar. Siliceous and metal oxides have affinities for polar compounds. Activated carbon is the most commonly used nonpolar adsorbent.

Silica gel and aluminum oxide preferentially adsorb water vapor from a emission control if the water content is greater than the organic vapor content. Also, these adsorbents disintegrate in the presence of liquid water; hence wet steam may not be used for desorption, but they can be used successfully in the drying of water-saturated solvents recovered by decantation.

The great advantage that activated carbon has over other adsorbents is its outstanding ability to recover organic solvents from low concentrations of gases even in the presence of water vapor. Vapors that can be adsorbed by activated carbon are listed in Table 4-3. Activated carbons are manufactured from coconut shells, fruit pits, coal, peat, and petroleum

Table 4-3.-REPRESENTATIVE GASES AND VAPORS SELECTIVELY ADSORBED BY ACTIVATED CARBON

1. acetaldehyde
2. acetone
3. benzene
4. isobutane
5. normal butane
6. normal butene
7. butyne
8. carbon dioxide
9. carbon disulfide
10. carbon tetrachloride
11. carbonyl sulfide
12. chloroform
13. cumene
14. cyclohexane
15. cyclohexanone
16. cyclopentadiene
17. dichloroethane
18. dichloroethylene
19. dimethyl formamide
20. ethane
21. ethanol
22. ethyl acetate
23. ethyl chloride
24. ethyl mercaptan
25. ethylene
26. ethylene oxide
27. freon 12
28. heptane
29. normal hexane
30. hexanol
31. hydrogen cyanide
32. hydrogen sulfide
33. isopentane
34. isoprene (methyl butadiene 1,3)
35. isovaleric acid
36. simulated kerosene ($C_{14}H_{30}$)
37. methane
38. methyl ethyl ketone
39. methyl mercaptan
40. mineral spirits
41. neopentane
42. normal pentane
43. perchloroethylene
44. propane
45. propylene
46. propyl mercaptan
47. pyridine
48. tetrahydrofuran
49. tetrahydrothiamine
50. toluene
51. trichloroethylene
52. vinyl chloride
53. metaxylene

residues.[37] The raw materials are first carbonized by selective oxidation in air at low temperature. Then the hard materials are crushed to size and activated directly to give dense carbon granules, and the softer materials are ground to a powder, formed into briquettes or pellets with a tar or pitch binder, calcined, crushed to size, and finally activated by heating to 1120 to 1220 K with steam, carbon dioxide, or flue gas.

4.3.1 Equipment Description

The main function of the adsorption equipment is to bring the gas and solid adsorbent into direct contact. Contact is achieved in either fixed, moving, or fluidized beds, set vertically or horizontally. The simplest equipment for a fixed-bed adsorber is a vertical cylindrical vessel fitted with perforated screens that support the carbon. Another type in the shape of a cone is shown in Figure 4-7; a commercially available, skid-mounted unit is shown in Figure 4-8. Moving-bed adsorbers actually move the adsorbent into and out of the adsorption zone. In fluidized-bed adsorbers, the solvent is adsorbed onto the carbon as air flows upward through a number of beds and fluidizes them; thus, solvent-free air is finally discharged through dust collectors at the top of the adsorber vessel. Fresh adsorbent which is fed onto the top tray of the adsorber, flows across the tray, over a weir, and down through a downcomer to the tray beneath; thus its solvent load increases progressively as it moves through the adsorber.

Adsorbers are classified as regenerative or nonregenerative. In regenerative systems the adsorbent is reactivated by desorption and the desorbed vapors are recovered for reuse or disposal. In nonregenerative systems, the adsorbent is replaced with fresh material and the displaced material usually is returned to the vendor for regeneration. Figure 4-9 is a sketch of a typical fixed bed adsorption system in which one adsorber

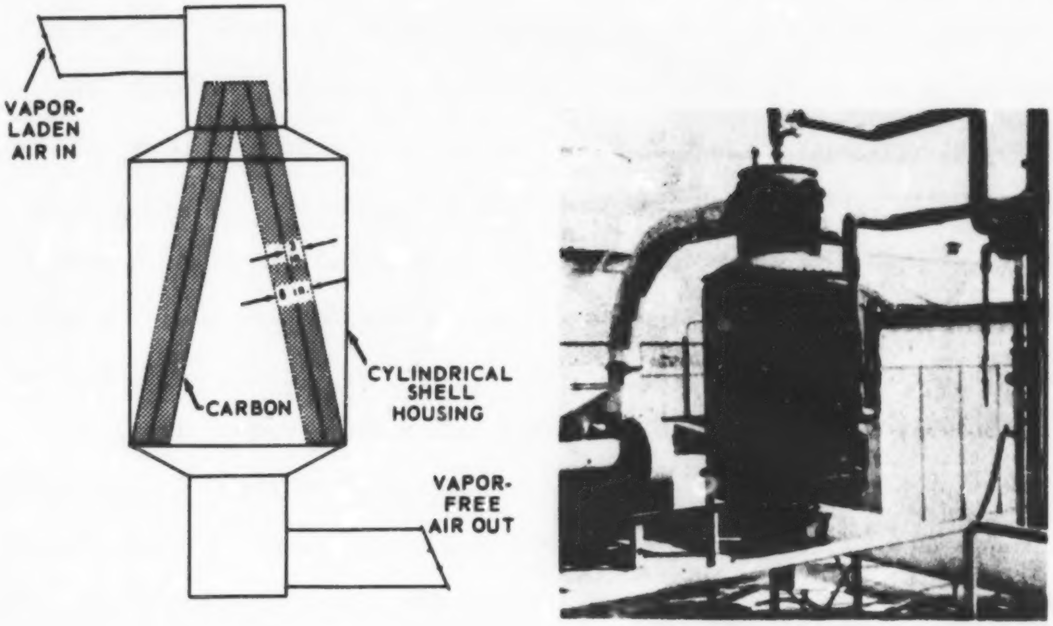

VAPOR-LADEN AIR IN
6 in.
CYLINDRICAL SHELL HOUSING
CARBON
VAPOR-FREE AIR OUT

Fig. 4-7. Diagrammatic sketch of vertical adsorber with two cones, permitting studies on different depths of carbon beds.

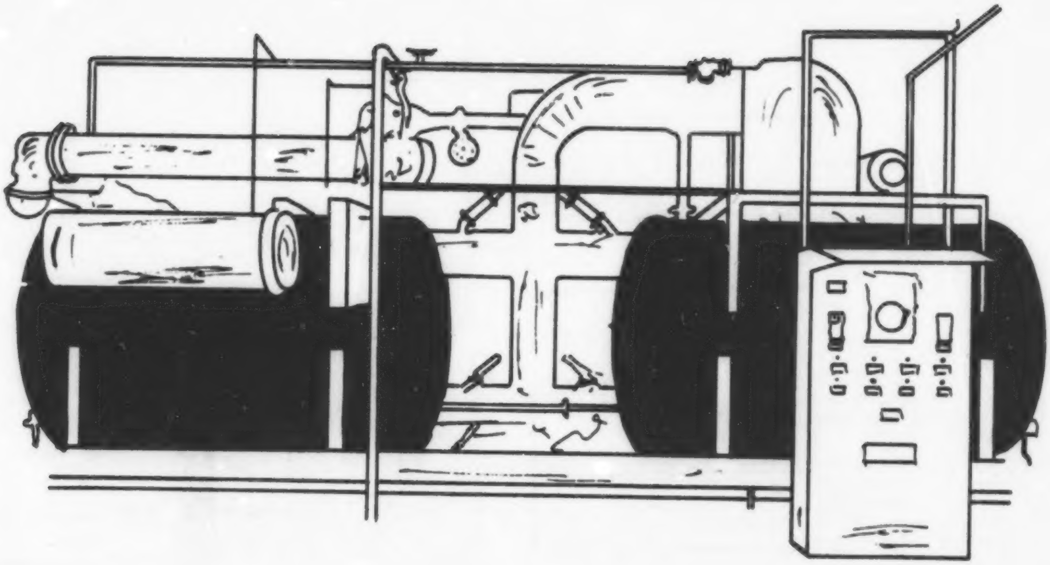


Fig. 4-8. Standard skid-mounted vapor recovery unit .

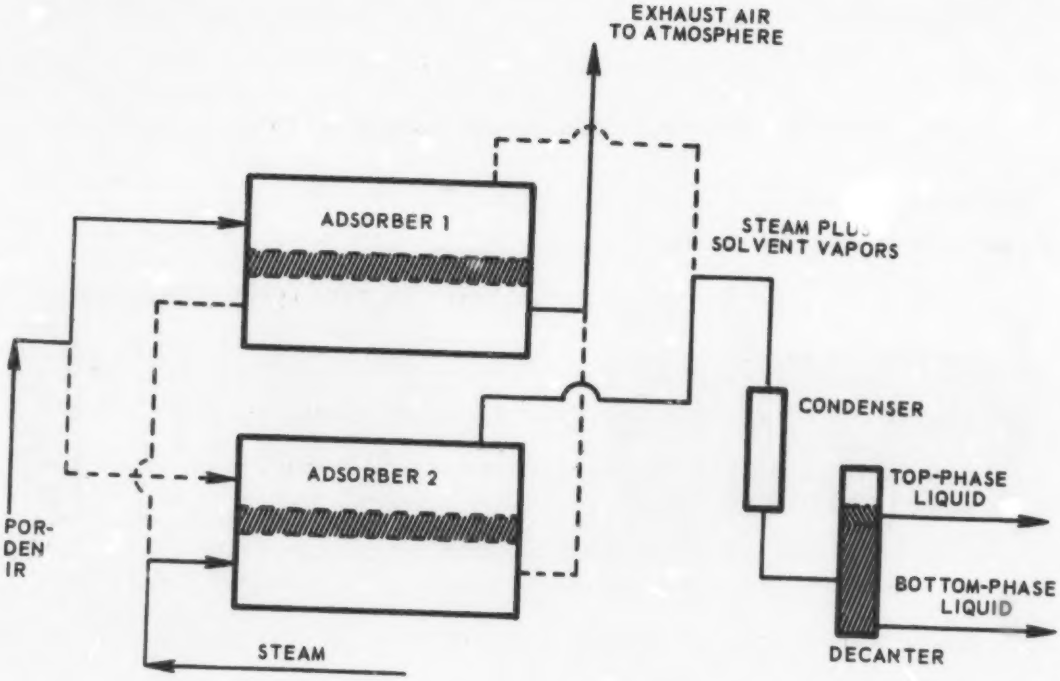

EXHAUST AIR
TO ATMOSPHERE
ADSORBER 1
STEAM PLU
SOLVENT VAPORS
CONDENSER
ADSORBER 2
TOP-PHASE
LIQUID
BOTTOM-PHASE
LIQUID
POR-
DEN
IR
STEAM
DECANTER

Fig. 4-6. Diagrammatic sketch of two-unit fixed-bed adsorber.

handles the vapor-laden stream while the other undergoes regeneration. An example of a system that requires one instead of two adsorbers is a spray-paint booth used only 6 hr/day and designed to extract the total emission but to be desorbed after the operating period.

4.3.2 Operational Factors

Fixed-bed, cone-shaped vertical adsorbers allow more surface contact area for gas flow, thus accommodating higher air rates at lower pressure drops than a flat bed of the same diameter can using the same total weight of adsorbent. This reduces the cost of moving the gases through the system.

Fluidized-bed adsorbers tolerate high loading of solvent on carbon, require less steam for desorption, and avoid the channeling problem sometimes encountered with fixed beds because the carbon circulation rate can be closely matched to the solvent feed rates in this type bed.

For continuous adsorption, systems must have two or more adsorbers. When the first, or onstream, bed approaches the breakpoint, the second adsorber, (which meanwhile has been regenerated) is placed on stream. The point at which the rate of adsorption of the more volatile component starts to decrease and its evaporation starts to increase is called a "breakpoint"--the point at which the higher-boiling component displaces the lower-boiling component. This procedure insures that the vapor is removed from the air continuously. After desorption, one adsorber must be adequately cooled before it is placed on stream again to prevent contact of organic vapors with a hot carbon bed, which may cause decomposition or partial oxidation and consequent discharge of odorous or irritating gases to the atmosphere.[37] For continuous large-scale operations, a fluidized and a moving bed are required. A single fixed-bed unit is satisfactory if process downtime is available for regeneration of the adsorbent.

After some period of usage, the adsorbent becomes saturated with the contaminant and will no longer function. When this occurs, it must be regenerated or replaced. One method is to raise the temperature of the adsorbent until the vapor pressure of the adsorbed gas exceeds atmospheric pressure, so that the adsorbed gas can be evolved and collecged at atmospheric pressure. The most common method is to withdraw the adsorbed gas in a stream of easily condensable gas (e.g., steam or an inert gas) so that the mixture can be condensed to recover the gas. Thus, the adsorbent is restored to activity, and the adsorbed material is removed for disposal or recovery.

If the gas or vapors to be adsorbed consist of several compounds, adsorption of the various components is not uniform. Generally, they are adsorbed in an approximate inverse relationship to their volatilities. At the start, when air containing a mixture of organic vapors is passed through a bed of adsorbent, the vapors are equally adsorbed; but as the amount of the higher-boiling constituent retained in the bed increases, the more volatile component revaporizes.

4.3.3 Typical Applications

Complete package adsorption systems are available from a number of manufacturers for use in gas-purification and other processes involving volatile solvents. Gas purification to remove small quantities of impurities, such as those listed, includes deodorizing of air, removing odors in ventilation systems of buildings, and the removing of dangerous toxic vapors from airstreams.

4.3.4 Recent Develcpments in Adsorption

Some progress has been made in providing methods for obtaining design data for fluid bed adsorbers. Lambert and Alley have developed a method employing post feed to a gas chromatograph packed with the desired adsorbant.[38] From data obtained using this type of column, the equilibrium constant, mass transfer and dispersion coefficients are calculated. A digital computer is used to simulate the adsorption column and validate the various parameters measured.

Electro desorption has been evaluated for benzene.[39] The benzene was adsorbed from an air stream saturated at 293 K. Desorption was accomplished by passing an electric current directly through the conductive adsorbent bed. The resistivity of the bed depends on the activated carbon used, its particle size, and its packing characteristics. More than 80 percent of the benzene introduced was recovered. Electric power passed during desorption was 516 MJ/m^3 carbon bed, heating the bed in about five minutes to 630 K. A unit recovering 0.5 kg of organic vapor would have a bed volume of about 2.8 dm^3 and the electric power cost would be about 3.5 to 4.4 cents per kilogram of liquid product. This organic vapor recovery process technique would appear to be generally applicable to hydrocarbons, solvents, and odorous materials.

Activated carbon remains the most widely applicable adsorbent for control of air pollutants. A prevalent hydrocarbon pollution problem is one where the emission stream contains multi-organics, most of which have little recovery value. Thus, a fundamental omission in the activated carbon technology area has been capacity data on many organics and combinations of the same. The Calgon Corporation has applied the Polanyi adsorption theory in a computer program which can be used to predict activated carbon capacity for many single components and mixtures. This has proved to be an aid in determining the technical feasibility of the adsorption approach.[40]

Where the recovery of adsorbed pollutants offers no economic advantage, alternative reactivation methods are being developed. One alternative is to reactivate the carbon with vacuum technique. By proper control, the purge stream can be virtually pure organic. In many cases these organics can then be condensed and recovered for reuse, perhaps as fuel. A second alternative is to use hot noncondensible gases to reactivate the carbon and then to direct this substantially concentrated purge stream to an incineration system.[41] These alternatives are being considered because of their possible cost advantages when compared to reactivation by conventional steaming and solvent recovery methods. A British cost analysis comparing carbon adsorption-incineration with adsorption-steam regeneration gives the estimated annual average cost of the former as $27 900 versus $46 100 for the latter.[42] The two systems were compared at equal capacity.

4.4 ABSORPTION

Absorption is the transfer of a soluble component of a gas mixture into a relatively nonvolatile liquid absorbent. The dissolved component may react chemically with the common absorbents—water, mineral oil, nonvolatile hydrocarbons, and aqueous solutions of oxidizing agents or alkalis.

Absorbers are used when gas and vapor concentrations are high; however, they are usually classified as production equipment, not emission control equipment. Low concentrations would require large expensive equipment to achieve high removal efficiencies.

Packed and spray towers (Figs. 11 and 12) are used more often than bubble-plate columns (Fig. 10) because they introduce lower pressure losses than the columns. These losses are important because large volumes of exhaust gases with relatively low concentrations of

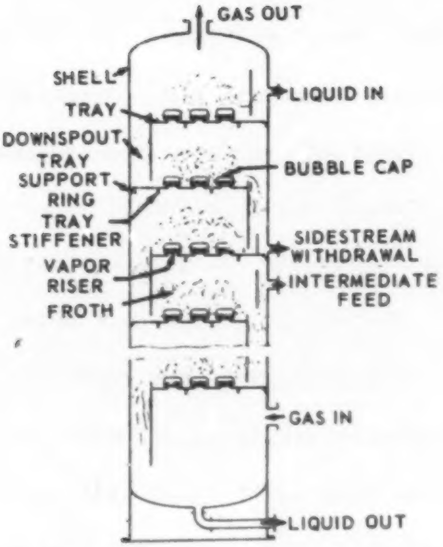

GAS OUT
SHELL
LIQUID IN
TRAY
DOWNSPOUT
TRAY SUPPORT RING
BUBBLE CAP
TRAY STIFFENER
SIDESTREAM WITHDRAWAL
VAPOR RISER
INTERMEDIATE FEED
FROTH
GAS IN
LIQUID OUT

Fig. 4-10. Schematic diagram of a bubble-cap tray tower.

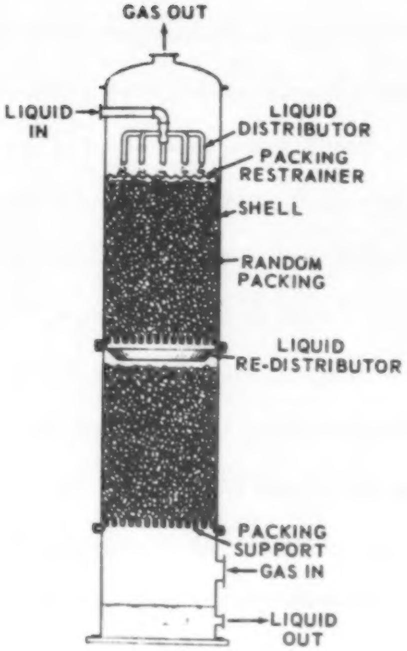

GAS OUT
LIQUID IN
LIQUID DISTRIBUTOR
PACKING RESTRAINER
SHELL
RANDOM PACKING
LIQUID RE-DISTRIBUTOR
PACKING SUPPORT
GAS IN
LIQUID OUT

Fig. 4-11. Packed tower.

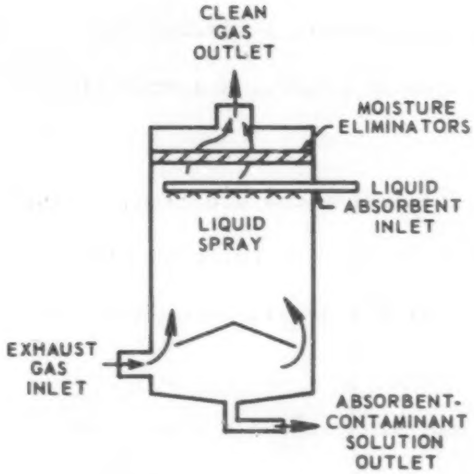

CLEAN GAS OUTLET
MOISTURE ELIMINATORS
LIQUID ABSORBENT INLET
LIQUID SPRAY
EXHAUST GAS INLET
ABSORBENT-CONTAMINANT SOLUTION OUTLET

Fig. 4-12. Spray tower.

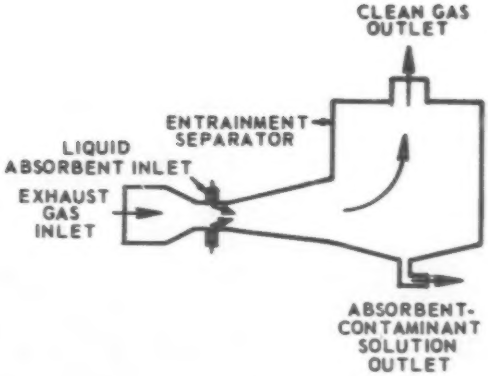

CLEAN GAS OUTLET
ENTRAINMENT SEPARATOR
LIQUID ABSORBENT INLET
EXHAUST GAS INLET
ABSORBENT-CONTAMINANT SOLUTION OUTLET

Fig. 4-13. Venturi scrubber.

contaminants are treated in many air pollution control installations. Spray towers have the advantage of being able to handle exhaust gases containing particulates without plugging; but, they are the least effective types of absorption equipment, because the fine liquid droplets, necessary for good contact, require spray nozzles operated at high pressure drop, tend to be entrained in the gas, and have to be separated. This is also true of Venturi scrubbers (Fig. 13).

4.4.1 Operational Factors

Absorption of a gaseous component by a liquid occurs when its concentration in the liquid is less than the equilibrium concentration of the gas. This departure of the liquid stream from equilibrium is the driving force for absorption.[43] As illustrated in Fig. 4-14, for a given liquid concentration, the gas concentration in the tower is always greater than the corresponding equilibrium concentration.

The rate of absorption depends on (1) the temperature, diffusivity, viscosity, and density of the substance; (2) the tower conditions, particularly the gas and liquid mass flow rates; and (3) the kind of packing. These factors and equilibrium data have been correlated to give two key measures of tower performance--the number of transfer units and the height

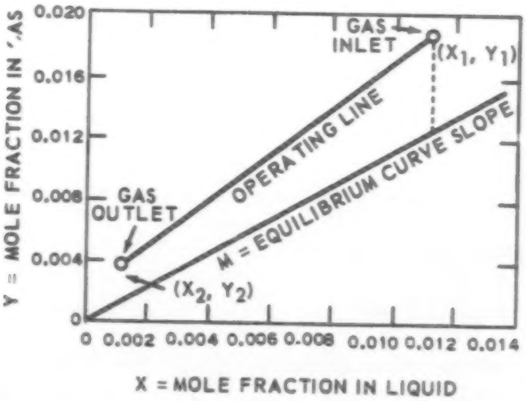


Fig. 4-14. Driving force for absorption.

of a transfer unit.[44] The number of transfer units is the number of times the driving force must be divided into the prescribed change in gas concentration; the height of a transfer unit is the depth of packing needed to effect one transfer unit. To estimate the depth of packing needed for the absorption, multiply the height of a transfer unit by the number of units. (Procedures for these calculations are given in the Air Pollution Engineering Manual.[1]) Because the effectiveness of a simple countercurrent tower is limited to one transfer unit, the enrichment of the liquid phase is equal to the driving force producing the enrichment. Packed towers can provide as many transfer units as practical. Generally, maximum absorption efficiency is achieved when gases and liquids are contacted in counterflow, but they can be contacted in parallel flow.

The packing should provide a large surface area and give enough void space when packed to permit good liquid flow. The material should be lightweight but should not break easily in handling; it should be chemically inert enough to prevent deterioration. Manufactured packing has various shapes, as shown in Figure 4-15. The most common is Raschig rings--hollow cylinders with external diameters equal to the lengths.

Usually, the emission concentrations are so low that the equilibrium curve and the operating curves are essentially straight lines. On the basis of these conditions, the size of an absorber can usually be made in three steps:

1. Determine the mass flow rates per square meter of tower area by using information supplied in Table 4-4 for the packing. These prescribed flows will permit the tower to operate without flooding. Use these values and the quantity of exhaust stream to be treated to determine the tower cross-sectional area.

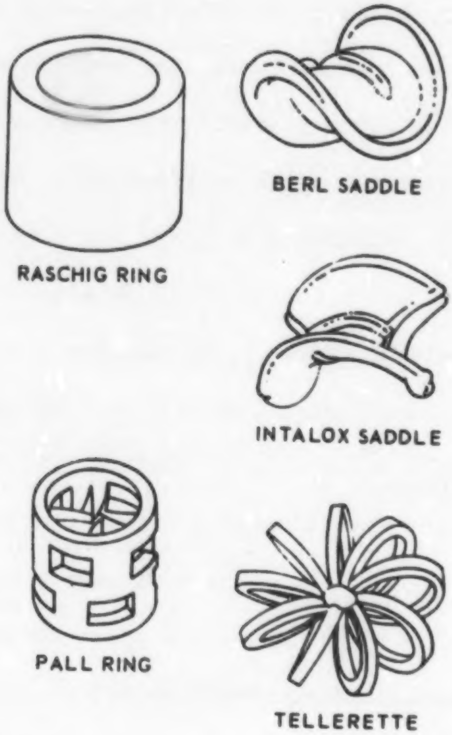

RASCHIG RING
BERL SADDLE
INTALOX SADDLE
PALL RING
TELLERETTE

Fig. 4-15. Common tower packing materials.

2. Determine the number of transfer units, N, by using Figure 4-16: First, convert the liquid and the gas flows, L and G, from kg/hr to moles/hr; then divide the ratio of liquid to gas by the slope of the equilibrium line m (as shown in Figure 4-14). The result is the "A" on each curve of Figure 4-16. The required ordinate is simply the outlet gas concentration (in mole fraction units) divided by the inlet concentration, since the incoming absorbent usually contains no absorbate ($x_2=0$).

3. Calculate the height of a gas-phase transfer unit, H_{tg} as follows:

$$H_{tg} = (C)(D)$$

where

$$C = \frac{\alpha(\text{gas rate, kg/hr-m}^2)^{\beta}}{(\text{liquid rate, kg/hr-m}^2)^{\gamma}} ;$$

and

$$D = \frac{(\text{gas viscosity, kg/hr-m})}{(\text{gas density, kg/m}^3)(\text{diffusivity, m}^2/\text{hr})}$$

and the diffusivity is that of the component in the gas stream. Then calculate the height of liquid-phase transfer unit, H_{tL}:

$$H_{tL} = \phi(E)(F)$$

where

$$E = \left[\frac{(\text{liquid rate, kg/hr-m}^2)}{(\text{liquid viscosity, kg/hr-m})}\right]^{\eta} ,$$

and

$$F = \frac{(\text{viscosity of the liquid, poise})}{(\text{liq. density, g/cm}^3)(\text{comp. liq. diffusivity, cm}^2/\text{s})} .$$

Values for α, β, γ, are given in Table 4-4, and values for ϕ and η are given in Table 4-5.

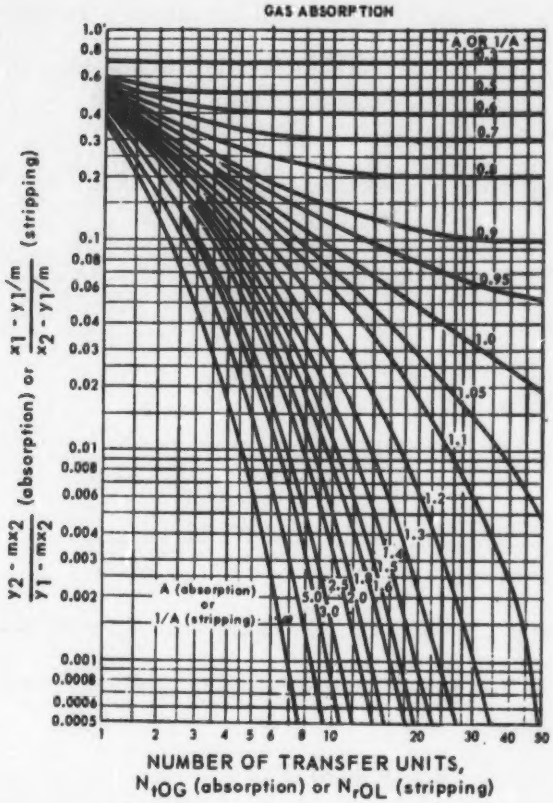


Fig. 4-16. Number of transfer units for absorbers or strippers with constant absorption stripping factor.

From these, the height of an overall transfer unit, H_{t0} is

$$H_{t0} = H_{tg} + H_{tL}/A.$$

Finally, multiply the number of transfer units by the height of each to get the packing height:

$$\text{Packing height} = (N)(H_{t0}).$$

The packed column requires a blower and motor to overcome its pressure drop. Pressure drop data show considerable variations, presumably due to differences in packing density. An empirical correlation has been developed to estimate the pressure drop per meter of packed height, using empirical constants fitted to the data for different types of packing.[44]

Table 4-4. – CONSTANTS FOR USE IN DETERMINING GAS-PHASE HEIGHTS OF TRANSFER UNITS

Packing	α	β	γ	Gas flow rate, kg/hr-m^2	Liquid flow rate, kg/hr-m^2
Raschig rings					
0.95 cm	0.71	0.45	0.47	977 to 2443	2433 to 7329
2.5 cm	2.52	0.39	0.58	977 to 3909	1954 to 2443
	2.62	0.32	0.51	977 to 2932	2443 to 21987
3.8 cm	8.13	0.38	0.66	977 to 3420	2443 to 7329
	0.79	0.38	0.40	977 to 3420	7329 to 21987
5.1 cm	1.29	0.41	0.45	977 to 3909	2443 to 21987
Berl saddles					
1.3 cm	19.76	0.30	0.74	977 to 3420	2443 to 7329
	0.21	0.30	0.24	977 to 3420	7329 to 21987
2.5 cm	0.61	0.36	0.40	977 to 3909	1954 to 21987
3.8 cm	1.81	0.32	0.45	977 to 4886	1954 to 21987
Partition rings					
7.6 cm	468	0.58	1.06	733 to 4397	14658 to 48860
Spiral rings(stacked staggered)					
7.6 cm single spiral	0.64	0.35	0.29	635 to 3420	14658 to 48860
7.6 cm triple spiral	6.55	0.38	0.60	977 to 4886	2443 to 14658
Drip-point grids					
No. 6146	1.21	0.37	0.39	635 to 4886	14658 to 31759
No. 6295	1.59	0.17	0.27	489 to 4886	9772 to 56189

Table 4-5. – CONSTANTS FOR USE IN DETERMINING LIQUID-PHASE HEIGHT OF TRANSFER UNITS

Packing	ϕ	η	L' range, kg/hr-m^2
Raschig rings			
0.95 cm	0.000326	0.46	1954 to 73290
1.3 cm	0.000714	0.35	1954 to 73290
2.5 cm	0.00230	0.22	1954 to 73290
3.8 cm	0.00255	0.22	1954 to 73290
5.1 cm	0.00262	0.22	1954 to 73290
Berl saddles			
1.3 cm	0.00139	0.28	1954 to 73290
2.5 cm	0.00123	0.28	1954 to 73290
3.8 cm	0.00131	0.28	1954 to 73290
Partition rings			
7.6 cm	0.0163	0.09	14658 to 68404
Spiral rings(stacked staggered)			
7.6 cm single spiral	0.00190	0.28	1954 to 73290
7.6 cm triple spiral	0.00243	0.28	14658 to 68404
Drip-point grids			
No. 6146	0.00354	0.23	17101 to 146580
No. 6295	0.00152	0.31	12215 to 107492

4.4.2 Typical Applications

The absorption technique is profitable as a step in petroleum and petrochemical operations in which a gas has a relatively high concentration of solvent vapor. From an air pollution standpoint, it has been used primarily to control inorganic rather than organic vapors because low concentrations of organic vapors require long contact time and large quantitites of absorbent; both requirements will increase costs unless the absorbent can be regenerated or the solution can be used as a process make-up stream to prevent the absorbent stream from being an additional disposal problem. In emission control applications, absorption is best used with other techniques such as incineration or adsorption.

4.4.3 Recent Developments in Absorption

While the status of the basic absorption technology has changed very little over the last five years, the role of the wet scrubber has gained significance relative to the packed and spray towers. This is due in part to the frequency of occurrence of the need to control particulates along with absorbable gaseous pollutants. Wet scrubbing for particulates depends principally upon inertial impaction as the collection mechanism. Various scrubber designs have been used for particulates larger than one micron with good results. Venturi scrubbers have been employed almost exclusively to provide the high gas velocities and dispersion of the liquid collecting phase necessary for control of sub-micron particles.[45] These scrubbers have been designed to utilize the resulting mists for absorption of gases and to provide for collection of the mists.[46]

4.5 CONDENSATION

Condensation is the collection of organic emissions by lowering the temperature of the gaseous stream to their condensation point. (Condensation by increasing pressure is possible but not usually practical for most air pollution control applications.) The temperature of a gasoline mixture is reduced to the saturation temperature, at which the vapor pressure equals the partial pressure of one of the constituents; thus, control is limited by the partial pressure of that constituent.

During condensation the partial pressure of the material remaining in the gas phase decreases rapidly, and complete condensation is not possible. For example, even at 273 K, toluene has a vapor pressure of about 798 N/m^2; at atmospheric pressure (101 kN/m^2), a gas stream saturated with toluene would still contain about 8 000 ppm of that gas. Thus, condensers must usually be followed by a secondary air pollution control system such as an afterburner, which treats the noncondensible gases and achieves a high degree of overall efficiency. For this reason, condensers have not been used as much as afterburners and adsorbers to control organic gas emissions.

4.5.1 Equipment Description

Condensers are of two types, contact and surface. In contact condensers, the gaseous stream is in direct contact with the cooling liquid, the condensed material mixing with the coolant; in a surface condenser, it is separated from the liquid by a metal wall. The use of a contact condenser can result in a water pollution problem, a factor that sometimes restricts the use of this type of condenser.

4.5.2 Operational Factors

The main factors to be considered in designing condensers are the types of compounds and their temperature, volume, concentration, vapor pressure, and specific heat. For contact condensers, the critical design factor is the amount of cooling water (kg/hr) needed to remove the heat (J/hr) from the condensing vapor:

$$\text{Heat} = (\text{vapor to be condensed})(\text{latent heat of vaporization}) + (\text{heat capacity of liquid})(\text{temperature of subcooling})\ ;$$

$$\text{Cooling water} = \frac{\text{heat to be removed}}{(\text{inlet water temperature} - \text{outlet water temperature})} .$$

About 6.8 kg (6.8 dm^3) of water is required at 288 K to condense 0.45 kg of steam at 373 K and to cool the condensate to 333 K. Dilution and subcooling of the condensate prevents release of volatile compounds. In a cylindrical contact-spray-chamber condenser, contact times of about 1 second and a cross-sectional velocity of about 2 to 2.6 m/s, and pressure drops of about 249 N/m^2 are typical.

For a surface condenser, the area of heat exchange is the critical factor:

$$A = \frac{Q}{UT_m}$$

where A = heat transfer area, m^2,
Q = heat to be removed, J/hr,
U = overall heat transfer coefficient, $J/hr\text{-}m^2\text{-}K$,
T_m = mean temperature difference, K.

The heat transfer coefficients on both the vapor and the liquid sides are required as well as the temperature and the amount of coolant available.

Solving this equation is difficult because U depends on many parameters of the condensing and cooling streams, but the value for U may be estimated from heat balance or may be determined experimentally.[47,48]

4.5.3 Typical Applications

Condensers have found a wide range of application in the organic chemical industry where their purpose has been to condense concentrated vapors in the primary process, rather than to reduce contaminant emissions. Applied in the primary process, they recover valuable products and reduce the volume of effluent gas.

Condensers used in the petroleum and chemical industries for concentrated vapors are classified as production equipment. High removal efficiency cannot be achieved with low concentrations. Condensers are, therefore, useful as preliminary devices followed by more efficient devices such as afterburners or adsorbers.

4.5.4 Recent Developments in Condensation

Condensation has usually found application in emissions control as a part of a system which employs other techniques; this tends to overcome its basic limitations. Nichols has used condensation, both direct contact and indirect contact, along with compression and scrubbing in a system developed to control emissions from gasoline and oil marketing terminals.[49] Vapor displaced during truck loading is piped to the recovery system where it is compressed to 0.31 MN/m^2 and cooled in a heat exchanger. The compressed vapor is bubbled through liquid gasoline which has been refrigerated to 250 K. The resulting cold compressed, supersaturated vapor is then sprayed with liquid from sprinklers. As the liquid droplets fall through the vapor, they collect the suspended gasoline. The system is reported to recover 95.6 percent of the gasoline in air vented from trucks during loading. Gases can, of course, be cooled offsite and transported to a control location for treatment.

This system has been applied to the largest distribution terminals in the warmer climates, where the vapor concentrations tend to lie outside the explosive range. In colder climates, it should be applied in such a way that the total system avoids risks of accumulating explosive mixtures.

4.6 PACKED FIBER BEDS

Condensed hydrocarbons in the form of particles may be collected in packed fiber beds.

4.6.1 Equipment Description

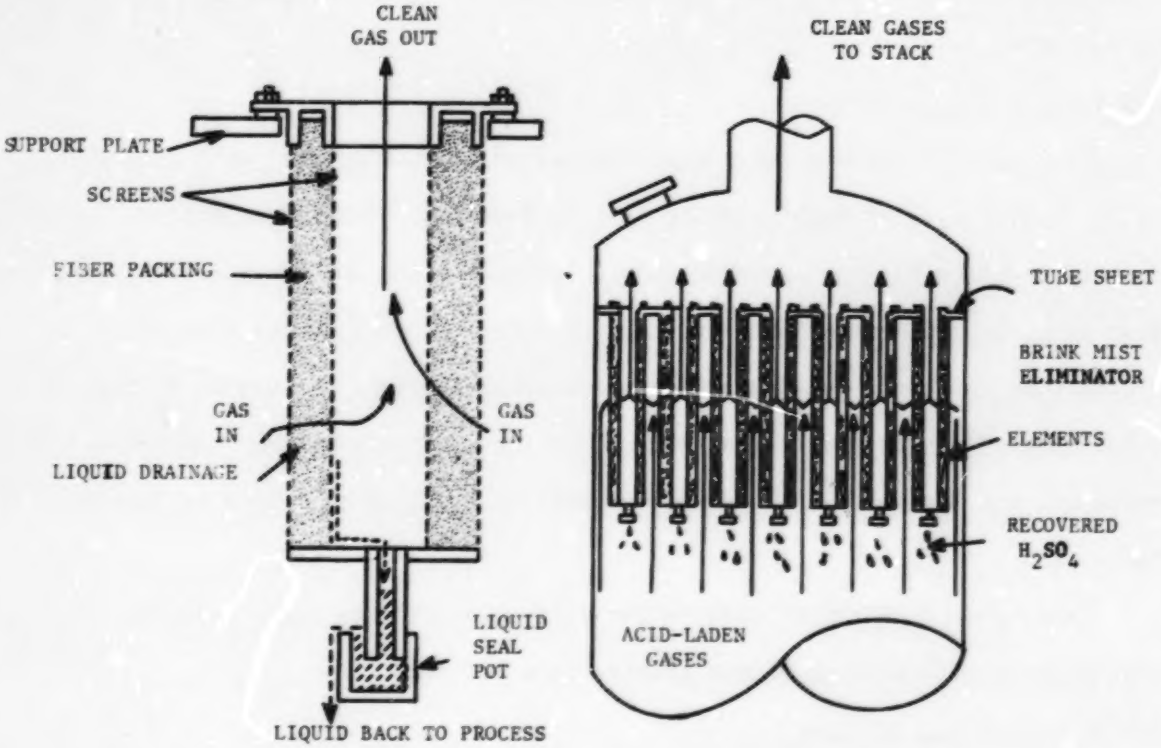
Mist eliminators-wet fiber mist eliminators may be either low velocity (0.03 to 0.15 m/s) or high velocity (1.5 to 2.6 m/s). The low-velocity design, Figure 4-17, has a packed bed of fibers between two concentric screens. Mist particles collect on the surface of the fibers, coalesce to form a liquid film that wets the fibers, and move horizontally and downward by the force of gravity and the drag of the gases; the liquid flows down the inner screen to the bottom of the element and through a liquid seal to a collection reservoir.

This type of filter is used in the collection of very fine condensed hydrocarbons with boiling points greater than 393 K.

4.6.2 Typical Application

Packed fiber beds have found a wide range of application for collection of very fine condensed aerosols (3/μm) and odorous emissions from rock-wool and glass-wool manufacture (phenol-formalin resin), offset printing factories, food industries, textile industries, asphalt and bitumen industries, plastic and rubber industries, and the chemical industries.

Packed fiber beds in emission control applications are best used in injunction with other techniques such as incineration, adsorption or electrostatic precipitation.


CLEAN
GAS OUT
SUPPORT PLATE
SCREENS
FIBER PACKING
GAS
IN
GAS
IN
LIQUID DRAINAGE
LIQUID
SEAL
POT
LIQUID BACK TO PROCESS
CLEAN GASES
TO STACK
TUBE SHEET
BRINK MIST
ELIMINATOR
ELEMENTS
RECOVERED
H_2SO_4
ACID-LADEN
GASES

a. LOW-VELOCITY FILTERING ELEMENT

b. MULTIPLE MOUNTING OF LOW-VELOCITY FILTERING ELEMENTS

Fig. 4-17. Low-velocity filtering elements.

4.7 ODOR CONTROL

The emission of odorous compounds forms a significant portion of the air pollution problem. It has been established that objectionable odors produce nausea, disturb sleep, and reduce property values. Most common odor emission sources are chemical and pulp manufacturers, petroleum and mineral refining, and foodstuff waste product and animal-rendering industries. The technology of odor evaluation and control has not advanced to keep pace with the growing problem; no suitable method or instrument is available for measuring odors objectively. Consequently, there is a marked deficiency in quantitative information on odor emissions from industrial sources.[50]

Since instruments have not been perfected to analyze odors objectively, subjective evaluation by a panel of human observers is used to estimate the character and intensity of industrial odors. There are mainly two methods by which the subjective evaluation is practiced: dilution and suprathreshold, or matching standard.[51] In both methods, the intensity of an odor is measured in terms of odor units. An odor unit is defined as the amount of odor necessary to contaminate 1 cubic foot of clean, odor-free air to the threshold level. The number of times a given volume of the gas sample has to be diluted with clean, odorless air to bring it to the threshold level (detected by 50 percent of a panel of observers) is the value of the intensity in odor units. The product flow rate times the odor intensity, gives the rate of odor emission.

Odor standards are under development in the United States. Now classified as non-criteria pollutants, odors would largely be controlled by state regulation. Federal recommendations under consideration at this time place a limit of 200 odor units per cubic foot on odor emissions from rendering plants.

The Manufacturing Chemists Association has published their findings on odor threshold research on 53 odorous commercial compounds. These are shown in Table 4-6.

These threshold values are generally below hygienic standards. Ammonia, for example, has an odor threshold of 0.21 ppm. This is below the 50 ppm maximal atmospheric concentration for 8 hours of exposure recommended by the Hygienic Guides Committee of the American Industrial Hygiene Association.[52]

Odor control techniques include process modification, ventilation and diffusion, chemical conversion, odorant capture, and masking or counteraction. Process modification aims at reducing odorants generation at the source. Chemical conversion includes oxidation and combustion. Odorant capture involves adsorption or absorption. Masking or counteraction involves sensory modification; it may occasionally be used alone but is usually applied where odorants occur in concentrations well below prescribed limits, based upon standards for health and safety.

Anderson and Posselt have investigated the chemical conversion of sulfur-containing organic odorants by reaction with potassium permanganate.[53] Using conditions similar to those existing in gas scrubbing devices, they fed odorant-containing gases into a 0.1 M (1.6 weight percent) permanganate solution buffered to a pH of 8.4 with dosium bicarbonate and into water. Table 4-7 shows the results obtained with 17 odorants the threshold odor numbers obtained with water alone are compared with those obtained using the permanganate.

Murthy and Eusebio compared the effectiveness of a number of reagents for odor control, feeding controlled concentrations of reagents to a scrubber and analyzing the exit gases with a gas chromatograph.[50] Their tests indicated that amines are efficiently removed by hydrochloric or

Table 4-6.- ODOR THRESHOLDS IN AIR[50]
(ppm by volume)

Chemical	Response	
	50 percent	100 percent
Acetaldehyde	0.21	0.21
Acetic acid	0.21	1.0
Acetone	46.8	100.0
Acrolein	0.1	0.21
Acrylonitrile	21.4	21.4
Allyl chloride	0.21	0.47
Amine, dimethyl	0.021	0.047
Amine, monomethyl	0.021	0.021
Amine, trimethyl	0.00021	0.00021
Ammonia	21.4	46.8
Aniline	1.0	1.0
Benzene	2.14	4.68
Benzyl chloride	0.01	0.047
Benzyl sulfide	0.0021	0.0021
Bromine	0.047	0.047
Butyric acid	0.00047	0.001
Carbon disulfide	0.1	0.21
Carbon tetrachloride (chlorination of CS_2)	10.0	21.4
Carbon tetrachloride (chlorination of CH_4)	46.8	100.0
Chloral	0.047	0.047
Chlorine	0.314	0.314
p-Cresol	0.00047	0.001
Dimethylacetamide	21.4	46.8
Dimethylformamide	21.4	100.0
Dimethyl sulfide	0.001	0.001
Diphenyl ether (perfume grade)	0.1	0.1
Diphenyl sulfide	0.0021	0.0047
Ethanol (synthetic)	4.68	10.0
Ethyl acrylate	0.0001	0.00047
Ethyl mercaptan	0.00047	0.001
Formaldehyde	1.0	1.0
Hydrochloric acid gas	10.0	10.0
Hydrogen sulfide (from Na_2S)	0.001	0.0047
Hydrogen sulfide gas	0.00021	0.00047

Table 4-6. -ODOR THRESHOLDS IN AIR--Continued

Chemical	Response	
	50 percent	100 percent
Methanol	100.0	100.0
Methyl chloride	[Above 10 ppm]	
Methylene chloride	214.0	214.0
Methyl ethyl ketone	4.68	10.0
Methyl isobutyl ketone	0.47	0.47
Methyl mercaptan	0.001	0.0021
Methyl methacrylate	0.21	0.21
Monochlorobenzene	0.21	0.21
Nitrobenzene	0.0047	0.0047
Perchloroethylene	4.68	4.68
Pehnol	0.021	0.047
Phosgene	0.47	1.0
Phosphine	0.021	0.021
Pyridine	0.01	0.021
Styrene (inhibited)	0.047	0.1
Styrene (uninhibited)	0.047	0.047
Sulfur dichloride	0.001	0.001
Sulfur dioxide	0.47	0.47
Toluene (from coke)	2.14	4.68
Toluene (from petroleum)	2.14	2.14
Tolylene diisocyanate	0.21	2.14
Trichloroethylene	21.4	21.4
p-Xylene	0.47	0.47

Table 4-7. -THRESHOLD ODOR NUMBER (T.O.N.) REDUCTION OF THIO COMPOUNDS[45]

Compound	T.O.N. H_2O	T.O.N. $KMnO_4$
CH_3-SO-CH_3	400	2
CH_3-S-CH_3	1 600	1
C_2H_5-S-C_2H_5	1 600	2
C_3H_7-S-C_3H_7	12 000	10[a]
C_3H_7-SH	3 300 000	160
C_4H_9-SH	200 000	33[a]
C_5H_{11}-SH	100 000	16[a]
C_6H_{13}-SH	85 000	10.5[a]
C_7H_{15}-SH	3 200	20[a]
C_8H_{17}-SH	3 500	6.5[a]
C_6H_5-SH	1 300	13[a]
CH_3-S-S-CH_3	1 500	1
C_2H_5-S-S-C_2H_5	1 200	4
C_3H_7-S-S-C_3H_7	3 000	10
C_4H_4S	4 000	13[a]
HS-CH_2COOH	65	1
HS-C_2H_4OH	30	1

[a] Improved odor characteristics.

sulfuric acid, mercaptans are best removed by sodium hydroxide (calcium hydroxide slurry may be better economically) aldehydes are best scrubbed with sodium or calcium bisulfites; all of these odorants are uniformly controlled by potassium permanganate, but permanganate is not the most efficient for any of them. The efficiency of permanganate depends on the pH of the solution and is maximum in the pH range of 8 to 10. The authors defined removal efficiency as the percent of the inlet odor removed by the same volume of reagent under identical conditions of contact time and reagent concentration.

Although activated carbon is widely used as an adsorbent for odor control, it has been shown to be a poor adsorbent for hydrogen sulfide, carbonyl sulfide, acetaldehyde, and some amines.[50]

Odor masking is the overpowering of a malodor by a stronger and initially more acceptable scent. The technique is not recommended; the "pleasant" odor may become objectionable itself upon continued exposure or become, in effect, a pollutant itself.

Odor counteraction, or sensory modification, is considered to be the phenomenon whereby odor intensity, however measured, is reduced by adding a non-chemically-reactive controlling agent to a malodor.[54] Proper and effective application of odor counteractants is usually feasible only after optimum use has been made of conventional control techniques and the odorant material has been reduced to the allowable concentration. Counteractants add to the total emissions; therefore, they should be biodegradable.[55] For many hydrocarbons and organic odorants there is a substantial spread between their odor recognition threshold and their maximum allowable concentration. Within this range, where many local pollution control regulations classify noxious odors as "nuisances" rather than as pollutants and where there is no toxicity problem to workers or others, it is often impractical or inordinately costly to collect and remove or destroy the residual malodorous emissions. It is in this quantitatively limited band of the gaseous emissions spectrum that odor counteraction can be practically and effectively employed.

Odor counteractants are generally formulated by manufacturers as proprietary products. They may include natural and synthetic essential oils and aromatics according to the complexity of the odor problem. Materials used include C_6-C_{12}-substituted phenyl ammonium salts. The components are usually GRAS ("generally recognized as safe") chemicals. Some manufacturers of proprietary counteractants supply both materials and necessary engineering services (e.g., Airkem Division, Air Wick Industries).[55]

4.8 PROCESS MODIFICATION

Printing plants present special problems for which thermal incineration has not proved to be a complete solution. Carruthers reports an investigation of the effects of kind of ink and kind of stock on emission from two 38-inch web presses.[56] Gloss-coated and matt-coated No. 45 paper were employed with inks containing 20 to 30 percent solvent (mostly C_{11}-C_{12} hydrocarbons). Increasing the amount of flame drying substantially altered the emissions: high-boiling hydrocarbons disappeared and low-boiling hydrocarbons (C_3-C_9) appeared. The glossy paper promoted burning and cracking of the solvent on the web so that less high-boiling hydrocarbons were emitted; the opposite effect was observed for matt-coated paper. The results indicate that by adjustment of heat in the dryer, smoke and odors from high-boilers and low-boilers, respectively, can be controlled.

Coke oven operation has been studied to determine how benzol losses could be reduced in the final coke oven gas. Marchenko analyzed a mathematical model of closed-cycle absorption-desorption processes in coke-oven-based benzol plants.[57] He concluded that benzol losses in the final coke oven gas could be minimized only by controlling the wash oil circulation rate. The optimum circulation rate was found to vary widely according to specific operating conditions; this indicates that a specific mathematical model should be constructed to optimize each given plant.

Coke oven emissions from charging operations (5 400 kg/day in large plants) have been controlled by a completely sealed pipeline charging system.[58] Coal no larger than 0.0254 m is fed to a flash-drying entrainment section of a preheater. Here particles are crushed to 3.2 mm size and heated to 640 K. Coal leaving the preheater goes to cyclones for collection of the dusts, which are fed by screw conveyors to charging bins. A portion of the gas from the cyclones is recycled back to the combustion chamber; the balance is sent to a wet scrubber. Since the system is completely sealed, emissions are kept from escaping to the atmosphere.

Nitrotoluene impurities in process water from trinitrotoluene plants have been extracted with toluene; this is indicated as an approach to control by recycling of these contaminants which are removed from the air. The plants considered use a Mahon fog filter system as an air pollution control system in the trinitrotoluene (TNT) process line. By a simple extraction technique, using a volume ratio of approximately 1 toluene to 150 Mahon fog filter wastewater, essentially all of the nitrotoluene impurities were removed from the wash water. The water is presently polluting streams in the vicinity of TNT manufacturing plants. Military-grade TNT can be prepared by nitration from these toluene extracts, which contain up to 6.4 percent nitrotoluenes. This procedure, however, cannot be used to eliminate the nitrotoluenes present in TNT red waters.

Solventless printing inks have been investigated by Bassemir.[59] Thermal curing inks are claimed to have very low vapor pressure at ambient temperatures and to be extremely stable on the ink distribution rollers. A small amount of effluent is still liberated although there are no visible emissions. Condensable effluents are reduced by as much as 85 percent. Radiation curing inks emit no effluents from the polymerization process and are completely stable on the rollers. Pot life is virtually indefinite when kept from exposure to ultraviolet light and the paper is not degraded by high temperatures.

Ethylene plant pressure relieving systems have been studied by Noles, whose work emphasizes the need for a well-designed pressure relieving system.[60] Increased demand for high-purity ethylene has resulted in the construction of larger and larger capacity single-train ethylene plants. These large single-train ethylene plants contain an enormous quantity of light hydrocarbons that must be handled safely during startup, normal operating, shutdown, and emergency conditions. The design of the pressure relieving system in Continental Oil Company's petrochemical plant in Lake Charles, Louisiana, is described. The disposal of vapors and liquids is discussed, as well as wet and dry flare systems, emergency conditions, relief valve discharge and flare header piping, metallurgy, the flare stack location and height, and thermal expansion and contraction.

Painting of automobiles and other metallic surfaces has been a continuing emissions problem—a solution to which is hoped for by General Motors with a new technique to be started in June 1972 at a Framingham, Massachusetts, assembly plant. Powder paint eliminates emission of solvents and the liquid and solid waste problems of paint sludge. Despite problems of durability and "orange peel," powder paint will be used in dark green and white on a three-car-an-hour pilot line. Powder will be sprayed electrostatically,then fused in a high velocity oven, sanded and returned to the oven for reflowing over scratches. The powder is a thermoplastic acrylic applied over electro-deposited primer, which itself is pollution free.

Electro-deposition (ELPO) sharply reduces solvent emissions. A former problem--excess paint flow during rinsing into waste which could contaminate sanitation--has now been solved with "ultra-filtration"; the filtrate flushes excess paint back into a closed loop for recycling. The probability that a Los Angeles rule which limits the photochemical solvent exhausted into the air from spray booths or ovens may be widely adopted has triggered a search for new chemistry in coatings (high temperature incineration has not worked). One possible approach is replacement of chromates, blamed for some fish kills; another is dispersion coatings (they reduce solvent and reduce ratios in top coats and are being used in some auto plants now). A third approach could be shorter bake cycles--or elimination of baking entirely. One possibility, the use of polyurethane paints, is not yet technically feasible.

4.9 MATERIAL SUBSTITUTION

Emission of organic air pollutants from some operations cannot be reduced by the installation of control equipment. For example, solvent evaporation from decorative and protective coatings of buildings and structures cannot be confined for disposal, and organic emissions from industrial surface-coating operations, vapor degreasing, drycleaning, certain electronic and electrical manufacturing procedures, and some rubber and plastic manufacturing procedures can be minimized but the cost may be prohibitive. An alternative to these "mechanical" techniques is to reformulate the solvent being used so that the emitted material is less reactive. Many solvents with more than the allowed amount of reactive materials have been reformulated by manufacturers with materials in the nonreactive group.

Photochemical reactivity is the tendency of organic compounds and nitrogen oxides in the atmosphere and in the presence of ultraviolet radiation (sunlight) and appropriate meteorological conditions, to undergo a series of chemical reactions that result in the various manifestations associated with photochemical air pollution: eye irritation, vegetation damage, and poor visibility. Theoretically, all organic compounds can be ranked according to their relative abilities to undergo photochemical reactions characteristic of smog. For many, the data are not available. For some, the ranking on the basis of their rates of disappearance during photolysis would differ from the ranking of the basis of their abilities to produce eye irritation, and these two rankings would differ from the ranking on the basis of their abilities to reduce visibility or their abilities to cause plant damage. Thus, no one classification of organic compounds according to a photochemical reactivity is correct for all occasions.[61,62] However, organic solvents can be divided into two groups, those that are photochemically reactive and those that are not. The reactive emissions are restricted; the non-reactive are not; unless flame contact, baking, or heat-curing is involved.

To date, two areas, Los Angeles County and San Francisco Bay Area, have defined reactivity and enacted regulations based on the chemical structure of specified materials. The definitions differ. The goals of the regulations differ: the San Francisco area seeks to limit emissions of very reactive materials; the Los Angeles area seeks to limit emissions of moderately reactive materials. To illustrate control by regulation, the principal provisions of both are given. Because the Los Angeles rule was a pioneering effort, information leading up to its adoption is given.

4.9.1 Rule 66 (Los Angeles)

Los Angeles County, because of its photochemical air pollution problem, enacted in 1966 a regulation to limit certain organic solvent emissions on the basis of reactivity. Rule 66, Section "k" of this rule[63] defines a photochemically reactive solvent:

> "... any solvent with an aggregate of more than 20 percent of its total volume composed of the chemical compounds classified below or which exceeds any of the following individual percentage composition limitations, referred to the total volume of solvent:
>
> (1) A combination of hydrocarbons, alcohols, aldehydes, esters, ethers, or ketones having an olefinic or cyclo-olefinic type of unsaturation: 5 percent;
>
> (2) A combination of aromatic compounds with eight or more carbon atoms to the molecule except ethylbenzene: 8 percent;
>
> (3) A combination of ethylbenzene, ketones having branched hydrocarbon structures, trichlorethylene, or toluene: 20 percent."

Section "a" limits the emissions from paint-baking ovens or heat-curing operations to 6.8 kg/day or requires that they be reduced by 85 percent, regardless of the type of solvent used.

Section "b" limits emissions from all other operations using photochemical reactive solvents to 18.2 kg/day or requires that they be reduced by 85 percent. Exempt from the provisions of "b" are: saturated halogenated hydrocarbons; perchloroethylene; applications of insecticides, pesticides, or herbicides; and the manufacture, transport, or storage of organic solvents.

Rule 66.1 prohibits the sale or use of architectural coatings that contain photochemically reactive solvents, as defined above.

Rule 66 provides that emission reduction must be accomplished by (1) incineration, with at least 90 percent of the carbon in the solvent being oxidized to carbon dioxide, or (2) adsorption, or (3) a method determined to be not less effective than (1) or (2).

The control techniques used to secure compliance with Rule 66 have been described by Krenz et al.[64] Among them are reformulation of the solvents used in the manufacture of paints and other protective coatings, use of direct-fired afterburners to control emissions from paint-baking ovens, use of trichloroethane and perchloroethylene in vapor degreasers, and reformulation of petroleum drycleaning solvents.

The experimental procedures and the evaluation of the results which led to Rule 66 have been described by Hamming.[65]

Extensive research by the Los Angeles control district demonstrated that many organic solvents are highly reactive when irradiated in the presence of nitrogen oxides, that some solvents produce even more ozone and eye irritation than irradiation of auto exhaust, and that partial oxidation of solvent vapors prior to their emission to the atmosphere enhances photochemical reactivity.

Several methods were used to determine the types and to estimate the quantities of organic solvents used in Los Angeles County. Preliminary screening was based on eye irritation tests—irradiating diluted portions of each solvent in a 0.05 m^3 flask. More extensive tests were performed in chambers of 33.4 m^3 capacity with solvent vapor concentrations of 2 to 16 ppm, 1 or 2 ppm nitrogen oxides, and irradiation times of 4 to 6 hours. The photochemical reactions tests were followed by analyses for hydrocarbons, nitric oxide, nitrogen dioxide, total oxidant, ozone, aldehydes, carbon monoxide, sulfur dioxide, and aerosols. The air pollution potential of a solvent or other test substance was based on photochemical effects:

1. eye irritation,
2. ozone formation,
3. aerosol formation,
4. total aldehyde formation,
5. effect on NO_x reaction,

Each solvent or mixture was compared, in terms of these criteria, with auto exhaust in various concentrations, with pure olefins, and with a "blank" chamber. If a substance equalled or exceeded the most dilute concentration of auto exhaust or pure olefins in their ability to produce any of the cited effects, it [illegible] labeled "reactive". If it failed to produce any of the cited effect[illegible] degree comparable with that produced by auto exhaust or pure ole[illegible] but greater than that produced by a "blank" (background)irradiation, it was "nonreactive" or "inert". The reactives were considered to probably need control; those labeled "slightly or moderately reactive" (intermediate between reactive and nonreactive) possibly to need control, but to a lesser extent than the reactive; and the nonreactives were regarded as needing little or no control.

Without regulation and control since enactment of Rule 66, uncontrolled emissions of organic solvents would have exceeded a calculated 0.54 Mkg/day by 1969. Because of the rule, they were reduced to 0.45 Mkg/day; many of these were either slightly reactive or nonreactive and, therefore, did not contribute greatly to the photochemical smog problem.

Future reductions may be confidently expected since it has been demonstrated that compliance with the Los Angeles County solvent control legislation can be achieved by (1) treatment of the organic emissions resulting from solvent usage, (2) converting to less photochemically reactive solvents, or (3) changing the process. An engineering permit system and an enforcement inspection program insure that control equipment to treat the effluent is designed for the required efficiency and operated in compliance with the law.

Rule 66 was designed to alleviate a condition in a specific area. Louis J. Fuller,[66] Air Pollution Control Officer of Los Angeles County, had this to say about its applicability to other areas:

> "It has been said that Rule 66 is the most talked about local air pollution legislation in the country. It is true that many communities both from this nation and abroad have inquired about it. I would, therefore, like to caution these communities first to learn the character and extent of their local problems, and then work to resolve them. This rule covers thousands of products, processes, combinations of equipment, production lines, and applications and is framed only for Los Angeles County. It may prove to be unrelated to other areas."

4.9.2 Regulation 3 (San Francisco Bay Area Air Pollution Control District)

In 1967, the San Francisco Bay Area Air Pollution Control District adopted a regulation to restrict the emissions of reactive organic materials--olefins, substituted aromatics, and aldehydes. (Not included as olefins were compounds in which all olefinic groups contain three or more halogen atoms.) A complying solvent was defined as any organic solvent which emits to the atmosphere organic compounds which on condensation contain 8 percent or less of reactive organic compounds provided that an additional 12 percent of the organic compounds from the emission may be monosubstituted aromatic compounds.[67] The purpose of this rule is to control the emissions of very reactive compounds only.[68] The rule limits organic emissions to 50 ppm, calculated as hexane, unless one of the following requirements is met:

1. A complying material is being used and no heat is applied, or heat is applied but the emission contains less than 5 ppm of aldehydes.
2. There are less than 5 percent reactives in the organic fraction of the emissions.
3. There are less than 4.5 kg of reactive, or less than 9.1 kg total, organic compounds emitted.
4. The reactives in the emission have been reduced by 85 percent overall.

If heat is applied and the emission contains more than 5 ppm aldehydes, the total organics must be less than 50 ppm, or the emission must meet one of requirements 2, 3, or 4 above.

Los Angeles County Air Pollution Control District classified the common solvents as reactive, slightly or moderately reactive, and nonreactive. Trichloroethylene was classified as slightly or moderately active.

Stanford Research Institute, sponsored by a group of manufacturers of trichloroethylene, conducted a 2-year smog-chamber study to develop additional data on the photochemical reactivity of trichloroethylene. The summary report by Katherine W. Wilson,[69] issued in September 1969, revealed that different experimental conditions and different indices of reactivity from those in the Los Angeles studies were used. On the basis of their results, the Stanford group attributed a low photochemical reactivity rating to trichloroethylene.

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5. EMISSION FACTORS FOR HYDROCARBON AND ORGANIC SOURCES

An emission factor is a statistical average of the rate at which pollutants are emitted from the burning (or processing) of a given quantity of material. (The factors can be based on some other meaningful parameter, such as the number of miles traveled in a vehicle.) To determine each factor, reliable data from a source or group of sources are gathered, correlated with information on process use, and tabulated. Either an average or a range of values is selected.

Some emission factors are based on limited data; others, on extensive data that are highly variable; and still others, on extensive, consistent data. It is, therefore, important that the precision of the data be evaluated before the factor is used for estimating emissions.

In general, the emission factors for hydrocarbon and organic air pollutants are not precise indicators for any single process even though the details of that process are known. They are more valid when applied to a number of processes.

Emission factors listed in Table 5-1 are for uncontrolled sources, except as noted in the table.

Table 5-1. - UNCONTROLLED EMISSION RATES FOR HYDROCARBONS AND ORGANIC SOURCES

Type of Emission Source	Emission Rate (g/kg)[1]
STATIONARY FUEL COMBUSTION SOURCE	
Bituminous Coal:	
Furnace greater than 30 MJ/s	
General	0.152
Wet bottom	0.152
Dry bottom	0.152
With cyclone	0.152
Furnace from 3 to 30 MJ/s	
Spreader stoker	0.502
Furnace less than 3 MJ/s	1.502
Hand-fired unit	10.002
Anthracite Coal:	
Dry bottom furnace	0.015
Overfeed stoker	0.1
Hand-fired unit	1.25
Fuel Oil:	
Power plant	g/m^3 360
Industrial/commercial unit	
Residual	g/m^3 480
Distillate	g/m^3 600
Domestic unit	g/m^3 600
Natural Gas:	
Power plant	kg/hm^3 750
Industrial process boiler	kg/hm^3 800
Domestic/commercial heating unit	kg/hm^3 300
Liquified Petroleum Gas (LPG):	
Industrial process furnace	
Butane	g/m^3 683
Propane	g/m^3 641
Domestic/commercial furnace	
Butane	g/m^3 228
Propane	g/m^3 204
Wood and Bark	1.25

See footnotes at the end of the table.

Table 5-1.—UNCONTROLLED EMISSION RATES FOR HYDROCARBONS AND ORGANIC SOURCES—Continued

Type of Emission Source	Emission Rate (g/kg)[1]
SOLID WASTE DISPOSAL	
Refuse Incinerator:	
Municipal multiple chamber	
Without settling chamber and water spray system	0.75
With settling chamber and water spray system	0.75
Industrial/commercial	
Multiple chamber	1.5
Single chamber	7.5
With control	Neg
Flue-fed	7.5
Modified flue-fed	1.5
Domestic single chamber	
Without primary burner	50.0
With primary burner	1.0
Pathological	Neg
Auto Body Incinerator:	
Without afterburner	kg/car 0.45
With afterburner	kg/car 0.21
Conical Burner:	
Municipal refuse	10.0
Wood	5.5
Open Burning:	
Municipal refuse	15.0
Automobile components	15.0
Horticultural refuse	
Agricultural field burning	10.0
Landscape refuse and pruning	10.0
Wood	2.0
MOBILE COMBUSTION SOURCE	
Gasoline-Powered Motor Vehicles	
Evaporation	kg/m^3 7.8
Crankcase	kg/m^3 1.6
Exhaust	
Urban	kg/m^3 32.4
Rural	kg/m^3 22.2

See footnotes at the end of the table.

Table 5-1.- UNCONTROLLED EMISSION RATES FOR HYDROCARBONS AND ORGANIC SOURCES--Continued

Type of Emission Source		Emission Rate (g/kg)[1]
Diesel:		
Truck or bus	kg/m³	5.2
Locomotive	kg/m³	7.3
Aircraft:		
Turbofan		
Jumbo jet	kg/engine-LTO	1.6
Long range	kg/engine-LTO	7.9
Medium range		
Without control	kg/engine-LTO	22.9
With smoke burner can	kg/engine-LTO	1.6
Turbojet	kg/engine-LTO	12.2
Turboprop	kg/engine-LTO	1.4
Turboshaft	kg/engine-LTO	0.32
Piston		
Transport	kg /engine-LTO	18.2
Light	kg /engine-LTO	0.23
Vessel:		
Steamship		
Underway	kg/km	0.059
In-berth	g/s	0.058
Motor ship		
Underway	kg/km	0.24
In-berth	g/s	0.19
EVAPORATION LOSS		
Dry-Cleaning Operation:		
Petroleum solvent		152.0
Synthetic solvent		
Without control		205.0
With average control		47.5
With good control		17.5
Surface-Coating Application		
Paint		560.0
Varnish and shellac		500.0
Lacquer		770.0
Enamel		420.0
Primer (zinc chromate)		660.0

See footnotes at the end of the table.

Table 5-1.-UNCONTROLLED EMISSION RATES FOR HYDROCARBONS AND ORGANIC SOURCES--Continued

Type of Emission Source			Emission Rate (g/kg)[1]
Storage of Petroleum Products:			
Storage of gasoline or finished petroleum product			
Fixed roof tank			
Breathing loss	kg/day/m^3 storage	0.05	
Working loss	kg/m^3 through put	1.32	
Floating roof tank			
Breathing loss	kg/day - tank	63.5	
Working loss	kg/m^3 through put	Neg	
Storage of crude oil			
Fixed roof tank			
Breathing loss	kg/day/m^3 storage	0.0375	
Working loss	kg/m^3 through put	0.96	
Floating roof tank			
Breathing loss	kg/day - tank	45.0	
Working loss	kg/m^3	Neg	
Gasoline Marketing			
Filling service station tank			
Splash fill	kg/m^3	1.44	
Submerged fill	kg/m^3	0.84	
50% splash fill and 50% submerged fill	kg/m^3	1.08	
Filling automobile tank	kg/m^3	1.44	
CHEMICAL PROCESS INDUSTRY			
Ammonia Manufacture:			
Purge gas from plant with methanator			45.0
Purge gas from plant with CO absorber and regenerator system			45.0
Carbon Black Manufacture:			
Channel process			5750
Thermal process			Neg
Furnace process			
Gas			900
Oil			200
Charcoal Manufacture			
Without chemical recovery plant			272
With chemical recovery plant			80.0

See footnotes at the end of the table.

Table 5-1.-UNCONTROLLED EMISSION RATES FOR HYDROCARBONS AND ORGANIC SOURCES--Continued

Type of Emission Source	Emission Rate (g/kg)[1]
Paint and Varnish Manufacture:	
Paint	15.0
Varnish	
Bodying oil	20.0
Oleoresinous	75.0
Alkyd	80.0
Acrylic	10.0
Phthalic Anhydride Manufacture:	
Without control	16.0
With catalytic combustion	5.5
Printing Ink Manufacture:	
General cooking	60.0
Oil cooking	20.0
Oleoresin cooking	75.0
Alkyd cooking	80.0
Synthetic Fiber Manufacture:	
Nylon	11.0
Dacron	3.5
FOOD AND AGRICULTURAL INDUSTRY	
Coffee Roasting:	
Direct-fired roaster	0.55
Indirect-fired roaster	0.55
Whiskey Aging . . . . kg/m^3 - yr 24.0	
Fish Meal Processing:	
Cooking fresh fish	0.15
Cooking stale fish	1.75
Meat Smoking:	
Without control	0.18
With control	0.08
Sugar Cane Field Burning . . . . g/m^2 33.6	

See footnotes at the end of the table.

Table 5-1.- UNCONTROLLED EMISSION RATES FOR HYDROCARBONS AND ORGANIC SOURCES--Continued

Type of Emission Source		Emission Rate (g/kg)[1]
METALLURGICAL INDUSTRY		
Coke Manufacture:		
Byproduct coking		
Charging		1.25
Coking cycle		0.75
Discharging		0.1
Beehive oven		4.0
MINERAL PRODUCTS INDUSTRY		
Asphalt Roofing Manufacture (Asphalt blowing)		0.75
Calcium Carbide Manufacture (Furnace room vents)		9.0
PETROLEUM INDUSTRY		
Petroleum Refinery:		
Boiler and process heater		
Oil-fired	g/m^3	471
Gas-fired	g/m^3	0.53
Fluid catalytic cracker (fresh feed)	g/m^3	682
Moving-bed catalytic cracker (fresh feed)	g/m^3	282
Compressor internal combustion engine (gas burned)	g/m^3	20.8
Blowdown system		
Without control	g/m^3	856
With control	g/m^3	14.3
Process drain (waste water)		
Without control	g/m^3	600
With control	g/m^3	22.8
Vacuum jet (vacuum distillation)		
Without control	g/m^3	370
With control	g/m^3	Neg
Cooling tower (cooling water)	kg/m^3	720
Miscellaneous losses (Refinery capacity, m^3)		
Pipeline valves and flanges	g/m^3	80
Vessel relief valves	g/m^3	31.4
Pump seals	g/m^3	48.5
Compressor seals	g/m^3	14.3
Air blowing, sampling, etc.	g/m^3	28.5

See footnotes at the end of the table.

Table 5-1. - UNCONTROLLED EMISSION RATES FOR HYDROCARBONS AND ORGANIC SOURCES--Continued

Type of Emission Source	Emission Rate (g/kg)[1]
WOOD PROCESSING	
Sulfate Pulping:	
Blow tank accumulator	0.05
Washers and screens	0.01
Multiple-effect evaporator	0.25
Recovery boiler and direct-contact evaporator	
Without control	6.0
With electrostatic precipitator	6.0
With venturi scrubber	6.0
Smelt dissolving tank	0.015
Lime kiln	
Without control	0.5
With scrubber	0.5
Turpentine condenser	0.005

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[1] Units other than g/kg are given at the end of the entries immediately preceding numerical values for uncontrolled rates; when controlled rates are known, they are listed by type of control applied.

REFERENCE

1. "Compilation of Air Pollutant Emission Factors." U.S. Dept. of Health, Education, and Welfare, Office of Air Programs, Research Triangle Park, N.C., AP-52, 1972.

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